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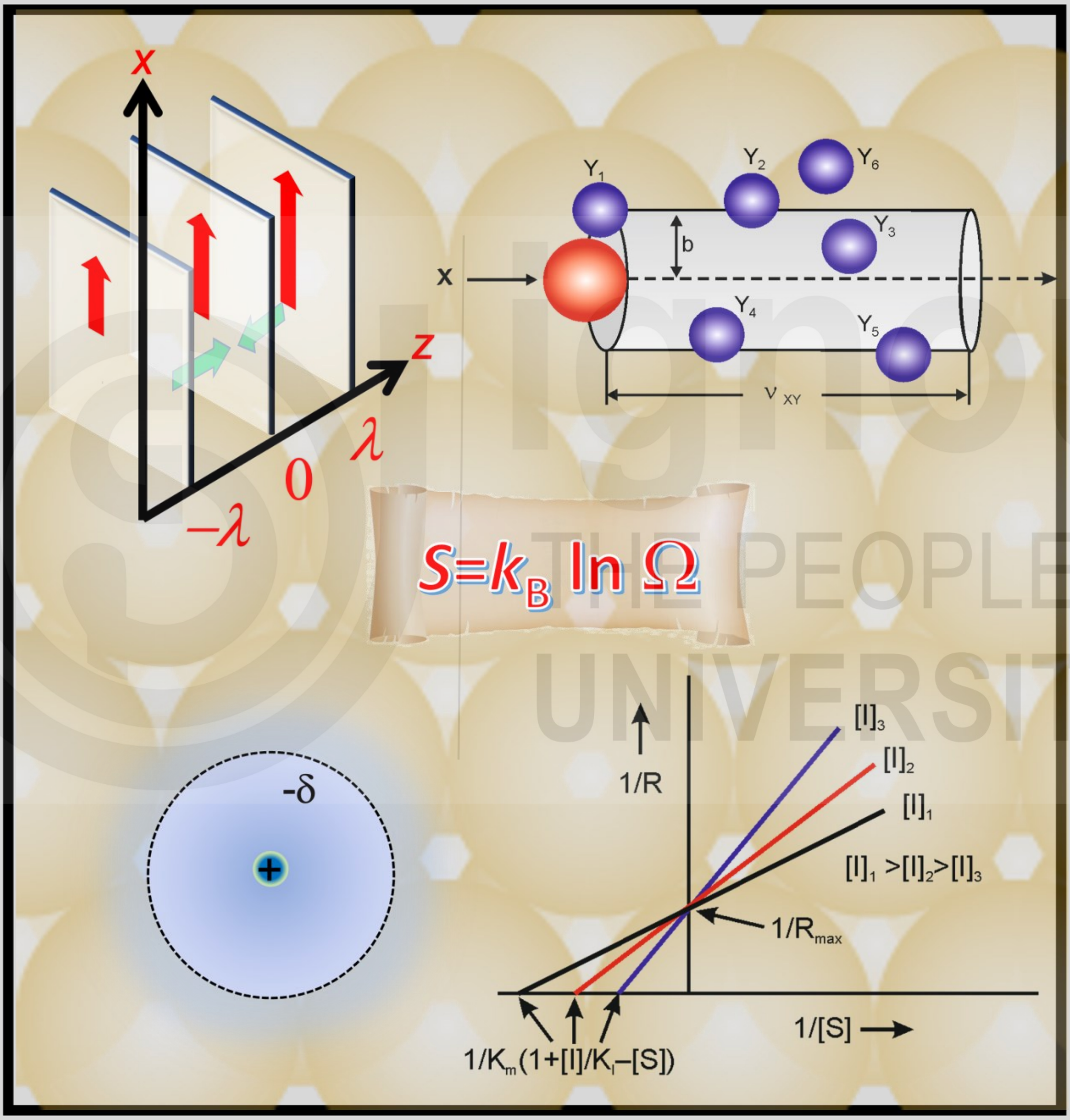
# MCH-013
# GENERAL PHYSICAL CHEMISTRY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$1/R_{max}$
1/[S] →
$1/K_m(1+[I]/K_I - [S])$

# Thermodynamics and Statistical Thermodynamics

## Block-1

Indira Gandhi National
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# MCH-013
# GENERAL PHYSICAL CHEMISTRY

Block

# 1

# THERMODYNAMICS AND STATISTICAL THERMODYNAMICS

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# Thermodynamics and Statistical Thermodynamics

The first block of volume-1 is titled “Thermodynamics and Statistical Thermodynamics” and contains four units. The first two units deal with two important areas of thermodynamics viz., Gibbs energy and Helmholtz energy and systems of variable composition. The remaining two units are dedicated to the introductory aspects of statistical thermodynamics.

The **first** unit titled, ‘Gibbs energy and Helmholtz energy” deals with two important concepts in thermodynamics viz., Gibb’s energy and Helmholtz energy. It strives to demonstrate the inadequacy of entropy as a criterion of spontaneity and argues, introduces, and establish Gibb’s energy and Helmholtz energy as the requisite criteria under the conditions of constant pressure and constant volume respectively.

The **second unit** concerns ‘systems of variable composition’ and covers partial molar properties, their determination and significance.  Herein it takes up the issue of the effect of change in composition of the system on its thermodynamic properties. Besides partial molar properties, the unit also deals with the concept and significance of chemical potential.

The **third** unit titled, “Introduction to statistical thermodynamics-I” serves to delineate the relationship between classical and statistical thermodynamics followed by introductory aspects of probability theory. It covers the concepts of probability, permutations, configurations, and probability distribution functions.

The **fourth** unit titled “Introduction to statistical thermodynamics-II” focuses on Boltzmann distribution function -the cornerstone of statistical thermodynamics, partition function and canonical ensemble.

## Objectives

After studying this block, you should be able to:

- derive an expression for the criterion for spontaneity for processes occurring under constant temperature and constant volume conditions and predict the spontaneity of reaction using them;
- derive an expression for the criterion for spontaneity for processes occurring under constant temperature and constant pressure conditions and predict the spontaneity of reaction using them;
- state the significance of Gibbs energy and Helmholtz energy;
- define partial molar quantities, outline their significance, and describe the method for the determination of partial molar volume;
- explain the term ‘chemical potential’, give its significance, and discuss the effect of temperature and pressure on it;
- discuss the relationship between classical and statistical thermodynamics;
- differentiate between permutation and configuration and calculate them for systems with small number of objects;
- state Stirling’s approximation, give its significance and establish its validity for systems with large number of particles;

- define microstate, configuration, weight of a configuration and dominant configuration and calculate them for a system;
- derive an expression for the Boltzmann distribution function give its significance and outline the constraints operative in it;
- briefly describe the Lagrange's method of undetermined multipliers; and
- derive expressions for translational, rotational, vibrational, and electronic partition

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UNIT 1

# GIBBS AND HELMHOLTZ FUNCTIONS

## Structure

1.1 Introduction
    Expected Learning Outcomes
1.2 Helmholtz function
    Helmholtz Energy Change: Criteria for Spontaneity and Equilibrium
    Physical Significance of Helmholtz Energy
1.3 Gibbs Function
    Gibbs Energy Change: Criteria for Spontaneity and Equilibrium
    Physical Significance of GibbsEnergy
    Relation between Helmholtz Energy and Gibbs Energy
1.4 Properties of Helmholtz energy and Gibbs energy
    Temperature and Volume Dependence of Helmholtz Energy
    Temperature and Pressure Dependence of Gibbs Energy
    Maxwell's Relations
1.5 Gibbs Energy Change for a Reaction
1.6 Summary
1.7 Terminal Questions
1.8 Answers

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## 1.1 INTRODUCTION

In the previous unit you have learnt about basic aspects of statistical thermodynamics. It provides a framework to quantitatively predict the behaviour of the bulk material in terms of the properties of microscopic particles. In this unit we will recall spontaneity and take up two important thermodynamic properties that serve as a criterion for the spontaneity and equilibrium of thermodynamic processes. You may recall that the two state functions viz., internal energy, and enthalpy that arise in the context of First law of thermodynamics do not serve as a criterion for spontaneity. On the other hand, the state function, entropy that arises while dealing with spontaneous processes does provide a criterion for spontaneity but is inconvenient to use.

We will begin the unit by discussing the difficulty in using entropy change as a criterion for spontaneity of a thermodynamic process. Herein, we will establish the need of new state functions for predicting the spontaneity based on the properties of the system only. Thereafter, we will take up the processes occurring under constant temperature and constant volume conditions and work out the criterion for spontaneity and equilibrium in terms of a new state function viz., Helmholtz energy. Then, we will work out the criterion for spontaneity and spontaneity for the processes occurring under constant temperature and constant pressure conditions. In this context we will define a yet another state function viz., Gibbs energy. Having introduced two important thermodynamic functions, we will discuss their physical significance and the interrelationship between the two.

This will be followed by a discussion on the properties of Helmholtz energy and Gibbs energy. Herein, we will take up the temperature and volume dependence of Helmholtz energy and temperature and pressure dependence of Gibbs energy. We will also take up Maxwell's relations and discuss their significance. Towards the end of the unit, we will be defining and evaluating the Gibbs energy change for a chemical reaction.

In the next unit we will take up systems of variable compositions.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- explain why entropy change is not a good criterion for spontaneity of a thermodynamic process?
- derive Clausius inequality and outline its significance;
- derive Helmholtz function as a criterion for spontaneity for processes occurring under constant temperature and constant volume conditions;
- give the criteria for spontaneity and equilibrium, for a process occurring under constant temperature and constant volume conditions, in terms of the sign and magnitude of $\Delta U$ and $\Delta S$;
- predict the spontaneity of processes occurring under constant temperature and constant volume conditions;
- derive Gibbs function as a criterion for spontaneity for processes occurring under constant temperature and constant pressure conditions;
- give the criteria for spontaneity and equilibrium, for a process occurring under constant temperature and constant pressure conditions, in terms of the sign and magnitude of $\Delta H$ and $\Delta S$;
- predict the spontaneity of a process occurring under constant temperature and constant pressure conditions;
- check whether a given thermodynamic system be able to attain equilibrium and under what conditions?
- derive the relation between Gibbs energy and Helmholtz energy;
- explain the change in Helmholtz function with the change in temperature and volume;

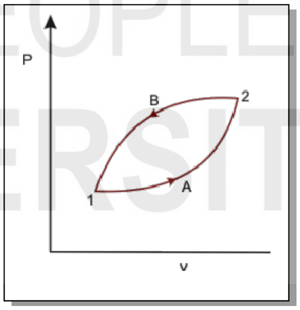
- explain the change in Gibbs function with the change in temperature and pressure;
- give the expression for Gibbs-Helmholtz equation and state its significance;
- derive Maxwell's relations and outline their significance; and
- define and calculate the Gibbs energy change for a reaction.

## 1.2 HELMHOLTZ FUNCTION

In your earlier classes you would have learnt about various aspects of energetics. You would recall that the First Law of thermodynamics concerns the conservation of energy. In the course of its study, we come across two important state functions viz., internal energy and enthalpy. You have also learnt about spontaneous processes i.e., the processes that occurs on their own under a given set of conditions without the aid of any external agency. As a chemist it is of interest to us to be able to predict the feasibility of a chemical reaction. However, the internal energy and enthalpy cannot predict the spontaneity of a process. This led to the introduction of a new state function viz., entropy that could serve as a criterion for spontaneity but could not be used effectively. Let us see why. However, before that let us derive two important relations that would help us in defining new state functions that may serve as criteria for spontaneity.

**Clausius inequality**

Let us consider two processes taking place between same initial and final states i.e., we go from state 1 to state 2 by two different routes. We assume that one of these processes takes place under reversible condition and the other one takes place under irreversible condition. Since internal energy is a state function, the change in internal energy for these processes will be equal i.e.,



$$\mathrm{d}U_{rev} = \mathrm{d}U_{irr} \qquad \text{...(1.1)}$$

You would recall that according to the first law of thermodynamics

$$\mathrm{d}U = \partial q + \partial w \qquad \text{...(1.2)}$$

In terms of the first law, we can write Eq. (1.1) as

$$\partial q_{rev} + \partial w_{rev} = \partial q_{irr} + \partial w_{irr} \qquad \text{...(1.3)}$$

Rearranging the expression, we get

$$\partial q_{rev} - \partial q_{irr} = \partial w_{irr} - \partial w_{rev} \qquad \text{...(1.4)}$$

Here, $\partial w$ represents the work done on the system and as you know that the work done on the system is positive and its magnitude during reversible process is greater than that during irreversible process, we can write,

$$|dw_{rev}| > |dw_{irr}| \qquad \text{...(1.5)}$$

Rearranging, we get

$$dw_{irr} - dw_{rev} > 0 \qquad \text{…(1.6)}$$

Substituting in Eq. (1.4), we get

$$dq_{rev} – dq_{irr} > 0 \qquad \text{…(1.7)}$$

Dividing the Eq. (1.7) throughout by *T,* we get

$$\frac{dq_{rev}}{T} - \frac{dq_{irr}}{T} > 0 \qquad \text{…(1.8)}$$

You would recall that for a reversible process, the change in entropy

$$dS = \frac{\partial q_{rev}}{\mathrm{T}} \qquad \text{…(1.9)}$$

So, we can write Eq. (1.8) as

$$dS - \frac{dq_{irr}}{T} > 0 \quad \text{or} \quad dS > \frac{dq_{irr}}{T} \qquad \text{…(1.10)}$$

The sum of entropy changes for the system and the entropy change of the surroundings increases in case of a spontaneous process.

Combining the expression for the entropy change during reversible, Eq. (1.9) and irreversible, Eq. (1.10)processes, we get

$$dS \geq \frac{dq}{T} \qquad \text{…(1.11)}$$

The Eq. (1.11) is known as **Clausius inequality**. This expression will be used later to arrive at the expressions for the spontaneity of thermodynamic processes under different conditions.

### Combined First and Second Law: The Fundamental Thermodynamic Equation

Once again, we take the expression for the First law of thermodynamics

$$dU = \partial q + \partial w \qquad \text{…(1.2)}$$

The fundamental thermodynamic equation, Eq. (2.14) applies to any change (reversible or irreversible) of a closed system that does not involve any non-expansion work.

We consider a case of a closed system with constant composition which undergoes a reversible change in such a way that only work of expansion is permitted. Since we are considering a reversible expansion, the opposing pressure ( $p_{\mathrm{ext}}$ ) would be equal to the pressure of the gas. Therefore, we can write,

$$dw_{\mathrm{rev}} = -p\,dV \qquad \text{…(1.12)}$$

From Eq. (1.9) for a reversible process we can write

$$\partial \mathrm{q}_{\mathrm{rev}} = T\,dS \qquad \text{…(1.13)}$$

Substituting from Eq. (1.12) and Eq. (1.13) in Eq. (1.2), we get

$$dU = T\,dS - p\,dV \qquad \text{…(1.14)}$$

This combined expression of the First and Second Laws is called the **fundamental thermodynamic equation**. It applies to any change of a closed system that does not involve any non-expansion work. Since internal energy is a state function, d$U$ is an exact differential. That is, its value is independent of the path. In other words, the value of d$U$ is same whether the change is brought about irreversibly or reversibly.

**Limited Utility of Entropy Change as a Criterion for Spontaneity.**

Now, let us take up the question of limited utility of entropy change as a criterion for spontaneity. You would have studied about entropy and spontaneity in your earlier classes. You would recall that the direction of an arbitrary spontaneous (irreversible)process is predicted by the following expression.

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{universe}} > 0 \qquad \ldots(1.15)$$

Whereas, for *reversible processes,* the following is true.

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{universe}} = 0 \qquad \ldots(1.16)$$

In other words, we can say that for an isolated system the total entropy of the universe *increases in an irreversible process* and remains *constant for reversible processes*. However, it never decreases. Thus, we see that entropy change does provide a criterion for establishing the spontaneity of a process. However, there is a limitation in applying this criterion to different systems. This is so because it requires calculating the entropy changes for the system as well as for the surroundings. Calculation of the entropy change for the system is relatively straightforward, but it is quite tedious (sometimes not practical) to calculate the entropy change for the surroundings. Therefore, we need a criterion for spontaneity that depends only on the properties of the 'system'. We would introduce such criterion in the next subsection.

For an isolated system the total entropy of the universe increases in an irreversible process and remains constant for reversible processes. However, it never decreases.

## 1.2.1 Helmholtz Energy Change: Criterion for Spontaneity and Equilibrium

You know that in chemistry the processes (chemical reactions) are carried out under constant temperature and constant pressure (or constant volume) conditions. Accordingly, we have two functions to predict the spontaneity of a process depending on reaction conditions. Let us begin with the processes carried out under constant temperature and constant volume conditions and deduce a function that can act as the criterion of spontaneity in such cases.

You know that according to the first law of thermodynamic, a process involving only mechanical work, (i.e., $p$-$V$ work) the change in internal energy is given by the following expression

$$\mathrm{d}U = \partial q - p\mathrm{d}V \qquad \ldots(1.17)$$

Let us consider the process wherein only heat flow is taking place between the system and the surroundings, and no mechanical work is involved. It implies that in this case, the volume is kept constant, that is, d$V$ = 0. Therefore, we can write

$$\mathrm{d}U = \partial q \qquad \ldots(1.18)$$

**Herman von Helmholtz (courtesy Wikipedia)**

According to Clausius inequality for a spontaneous flow of energy between the system and the surroundings, $\mathrm{d}S \geq \dfrac{\partial q}{T}$. i.e.,

$$TdS \geq \partial q \qquad \ldots(1.19)$$

Comparing Eqs.(1.18 and 1.19) we can write

$$dU \leq TdS \quad \text{or} \quad dU - TdS \leq 0 \qquad \ldots(1.20)$$

Since, $U$ and $S$ are state functions, a combination of two state functions will also be a state function. We can introduce a new state function as,

$$A = U - TS \qquad \ldots(1.21)$$

This Helmholtz energy was earlier known as Helmholtz free energy.

$A$ is known as **Helmholtz function** in honour of German physicist Hermann Ludwig Ferdinand von Helmholtz who had developed this concept. Since the internal energy and the term $TS$ has the dimensions of energy $(\text{K JK}^{-1} = \text{J})$, Helmholtz function $A$ will have the dimensions of energy, therefore it is referred to as **Helmholtz energy** and its SI unit is Joule. When the process is carried out under constant temperature condition, the change in Helmholtz energy is given by the expression

$$dA = dU - TdS \qquad \ldots(1.22)$$

$(dA)_{T,V} \leq 0$ serves as the criteria for spontaneous change and equilibrium for a process taking place at constant temperature and volume.

Comparing Eqs. (1.20) and (1.22) we get

$$(dA)_{T,V} \leq 0 \qquad \ldots(1.23)$$

We had initially assumed a spontaneous heat flow at constant volume and have applied the constant temperature condition on Eq. (1.21). Thus, the Eq. (1.23) provides a criterion for the *spontaneity and equilibrium for a process taking place at constant temperature and volume.* Thus, under the conditions of constant temperature and volume, a process will be spontaneous if it is accompanied by a decrease in Helmholtz energy ($\Delta$A<0) and would continue to be so till there is a decrease in Helmholtz energy. When it reaches a state of minimum Helmholtz energy such that there is no further change i.e., $\Delta A = 0$, the system will be at equilibrium.

The spontaneous processes are always irreversible in nature and have $\Delta A < 0$. Whereas for a reversible process, the system is always at equilibrium, and $\Delta A = 0$ .

For a finite change, the Eq. (1.22) can be written as

$$\Delta A = \Delta U - T\Delta S \qquad \ldots(1.24)$$

For a finite change taking place at constant temperature and volume, the criterion of spontaneity and equilibrium is given as

$$(\Delta A)_{T,V} \leq 0 \qquad \ldots(1.25)$$

### Conditions for Spontaneity and Equilibrium

We have shown that for a process to be spontaneous under constant temperature and constant volume conditions the Helmholtz energy should decrease($\Delta$A<0). This implies that for a non-spontaneous process the Helmholtz energy will increase. This means that the non-spontaneous process will be spontaneous in the reverse direction. The question then arises that what happens when there is no change in Helmholtz energy. In such cases, the process will neither go in the forward direction nor in the backward direction. That is, the system will be at equilibrium when there is no change in the Helmholtz energy i.e., $(\Delta A)_{T,V} = 0$

Combining Eq. (1.24) and the criteria of spontaneity ($\Delta A<0$) we find that the spontaneity of the process at constant temperature and constant volume depends on the combination of change in internal energy and the change in entropy of the system. That is, for a spontaneous process

$$\Delta U - T\Delta S < 0 \qquad \ldots(1.26)$$

There are several different combinations of internal energy change and entropy change possible for a given process. Let us now see whether and under what conditions the process will be spontaneous for each such combination of $\Delta U$ and $\Delta S$.

**Case 1:** $\Delta U < 0$ and $\Delta S > 0$

In this case, the value of $\Delta U - T\Delta S$ will be negative for all temperatures; hence, the process will be spontaneous at all the temperatures.

**Case 2:** $\Delta U > 0$ and $\Delta S < 0$

In this case the value of $\Delta U - T\Delta S$ will always be positive; hence, the process will never be spontaneous.

**Case 3:** $\Delta U < 0$ and $\Delta S < 0$

In this case, $\Delta U$ will be negative and $T\Delta S$ will be positive. At a certain temperature the magnitude of these will be equal i.e., $|\Delta U| = |T\Delta S|$ and $\Delta A = 0$. At this temperature the system will be at equilibrium. This temperature may be called as equilibrium temperature and can be calculated as

$$T = \frac{|\Delta U|}{|\Delta S|} \qquad \ldots(1.27)$$

Such a process can be spontaneous only when the magnitude of $\Delta U$ *is more than* $T\Delta S$, i.e., $|\Delta U| > |T\Delta S|$. This condition will be met at temperatures lower than the equilibrium temperature and the process will be spontaneous. At temperatures higher than the equilibrium temperature, $|T\Delta S|$ will be greater than $|\Delta U|$, and the process will be non-spontaneous.

**Case 4:** $\Delta U > 0$ and $\Delta S > 0$

In this case, both $\Delta U$ and $T\Delta S$ will be positive. Here again, at a certain temperature the magnitude of these will be equal i.e., $|\Delta U| = |T\Delta S|$ and $\Delta A = 0$. At this temperature the system will be at equilibrium and this temperature can be calculated using Eq. (1.27)

Such a process can be spontaneous only when the magnitude of $\Delta U$ is less than $T\Delta S$. That is

$$|\Delta U| < |T\Delta S| \qquad \ldots(1.28)$$

This condition will be met at temperatures higher than the equilibrium temperature and the process will be spontaneous. At temperature slower than the equilibrium temperature, $|\Delta U|$ will be greater than $|T\Delta S|$, and the process will be non-spontaneous.

**Case 5:** $\Delta S = 0$

In such cases, the process will be spontaneous only for exothermic processes, that is, $\Delta U < 0$ .Such a process will be at equilibrium when $\Delta U = 0$.

**Case 6:** $\Delta U = 0$

In such cases, the process will be spontaneous only when $\Delta S > 0$ .Such a process will be at equilibrium when $\Delta S = 0$ .

The conditions for spontaneity and equilibrium for different combinations of $\Delta U$ and $\Delta S$ are compiled in Table 1.1

**Table 1.1: The conditions for spontaneity and equilibrium for different combinations of $\Delta U$ and $\Delta S$.**

| **S. No.** | **Combination of $\Delta U$ and $\Delta S$ .** | **Condition for spontaneity** | **Condition for equilibrium** | **Remark** |
|---|---|---|---|---|
| 1 | $\Delta U < 0$ and<br>$\Delta S > 0$ | $\Delta U - T\Delta S < 0$ | $\Delta A = 0$ | Spontaneous at all temperatures; equilibrium not observed |
| 2 | $\Delta U > 0$ and<br>$\Delta S < 0$ | $\Delta U - T\Delta S < 0$ | $\Delta A = 0$ | Nonspontaneous at all temperatures; equilibrium not observed |
| 3 | $\Delta U < 0$ and<br>$\Delta S < 0$ | $\lvert\Delta U\rvert > \lvert T\Delta S\rvert$ | $\lvert\Delta U\rvert = \lvert T\Delta S\rvert$ | Equilibrium at<br>$T = \frac{\lvert\Delta U\rvert}{\lvert\Delta S\rvert}$<br>Spontaneous at temperatures lower than the equilibrium temperature |
| 4 | $\Delta U > 0$ and<br>$\Delta S > 0$ | $\lvert\Delta U\rvert < \lvert T\Delta S\rvert$ | $\lvert\Delta U\rvert = \lvert T\Delta S\rvert$ | Equilibrium at<br>$T = \frac{\lvert\Delta U\rvert}{\lvert\Delta S\rvert}$<br>Spontaneous at temperatures higher than the equilibrium temperature |
| 5 | $\Delta S = 0$ | $\Delta U < 0$ | $\Delta U = 0$ | Spontaneous only for exothermic processes |
| 6 | $\Delta U = 0$ | $\lvert\Delta S\rvert > 0$ | $\Delta S = 0$ | The entropy must increase for the process to be spontaneous |

Let us take an example to see how we can predict the spontaneity of a process by computing its Helmholtz energy change by using the temperature and the data on change in internal energy and change in entropy.

**Example1:** During an isochoric, isothermal process taking place at 25°C, the internal energy of the system decreased by 20 kJ mol$^{-1}$ and the entropy increased by 50 J K$^{-1}$mol$^{-1}$. Calculate the change in Helmholtz energy. Will the process be spontaneous?

**Solution:** The process is taking place at constant volume and constant temperature.

We are given: $\Delta U = -20\,\text{kJ mol}^{-1} = -20 \times 10^{3}\text{ J mol}^{-1}$

$$\Delta S = 50\text{ J K}^{-1}\text{mol}^{-1}$$

$$T = 25^{\circ}\text{C} = 298\,\text{K}$$

We know that the change in Helmholtz energy = $\Delta A = \Delta U - T\Delta S$

Substituting the values of $T$ , $\Delta U$ and $\Delta S$ in the above expression, we get

$$\Delta A = -20000\text{ J mol}^{-1} = -(298\,\text{K} \times 50\,\text{JK}^{-1}\text{mol}^{-1})$$

$$= -34900\text{ J mol}^{-1} = -34.9\,k\text{JK}^{-1}\text{mol}^{-1})$$

Since the Helmholtz energy change has a negative sign, that is Helmholtz energy is decreasing, therefore, the process will be spontaneous.

Having learnt about the criterion for spontaneity of the processes occurring under constant temperature and constant volume conditions in terms of Helmholtz energy change. Let us now see the physical significance of Helmholtz energy.

## 1.2.2 Physical Significance of Helmholtz Energy

As per Eq. (1.22) the change in Helmholtz energy is defined as

$$dA = dU - TdS \qquad \ldots(1.22)$$

We can recall the expressions for the first law of thermodynamics as under

$$\text{d}U = \partial q + \partial w \qquad \ldots(1.2)$$

The symbol *A* for Helmholtz energy is derived from German word, ‘Arbeit’ meaning work.

As per Eq. (1.13) for a system undergoing a reversible process according to the second law of thermodynamics, we can write

$$\partial \text{q}_{\text{rev}} = TdS \qquad \ldots(1.13)$$

Combining the expressions for the first and second law we can write

$$\text{d}U = T\text{d}S + \partial w_{rev} \qquad \ldots(1.29)$$

Substituting the expression for $\text{d}U$ in Eq. (1.22) we get,

$$dA = TdS + \partial w_{rev} - TdS \qquad \ldots(1.30)$$

$$dA = \partial w_{rev} \qquad \ldots(1.31)$$

According to Eq. (1.31), the change in Helmholtz energy is equal to the work done during isothermal reversible process. When the Helmholtz energy decreases, the value of $w_{rev}$ will be negative indicating that the work is done by the system. Therefore, *the decrease in Helmholtz energy is equal to the work done by the system during isothermal reversible process. This work includes all the types of work that the system can do. Since Helmholtz energy change is related to the maximum amount of work that can be obtained from a system, it is also known as* ***work function****.*

In the previous section we have studied that the criterion for spontaneity and equilibrium for a process under constant temperature and volume conditions can be given in terms of change in Helmholtz energy. However, in chemistry we generally study the process under constant temperature and constant pressure conditions as these are easier to maintain in the laboratory. Let us take up the case of spontaneity of a process under constant temperature and constant pressure conditions and determine a suitable criterion for the same.

## 1.3 GIBBS FUNCTION

Let us consider spontaneous heat flow taking place between the system and the surrounding at a constant pressure. You know that such a heat flow is equal to the change in enthalpy of the system, i.e.,

$$\mathrm{d}H = \partial q_p \qquad \ldots(1.32)$$

Using Clausius inequality, Eq. (1.11)we can write,

$$T\mathrm{d}S \geq \partial q \qquad \ldots(1.33)$$

Combining Eq.(1.32) and Eq. (1.33) we can write

$$T\mathrm{d}S \geq \mathrm{d}H \qquad \ldots(1.34)$$

It can be rearranged as

$$\mathrm{d}H - T\mathrm{d}S \leq 0 \qquad \ldots(1.35)$$

The Eq. (1.35) holds for a process taking place under constant temperature and constant pressure conditions. Since the left-hand side of the equation is a combination of two state functions, *H* and *S*, it will also be a state function. This combination is defined as a new state function called Gibbs function or **Gibbs energy** in honour of American chemist J. W. Gibbs who first came up with a relation to predict spontaneity of a process. It is represented as G and mathematically defined as:

$$G = H - TS \qquad \ldots(1.36)$$

Since enthalpy $(H)$ and $TS$ term $(\mathrm{K\,JK^{-1}=J})$, both have units of energy, *G* also will also have the units of energy, hence the name **Gibbs energy**. The SI units of Gibbs energy is Joule. When the temperature is kept constant, the infinitesimal change in Gibbs energy can be written as

$$dG = dH - TdS \qquad \ldots(1.37)$$

Eq. (1.35) is valid for the processes taking place under constant temperature and constant pressure conditions. Comparing Eq. (1.35) and Eq.(1.37) we can write that *for a process taking place at constant temperature and pressure, the Gibbs energy change of the system is less than or equal to zero.*

$$(\mathrm{d}G)_{T,p} \leq 0 \qquad \ldots(1.38)$$

## 1.3.1 Gibbs Energy: Criteria for Spontaneity and Equilibrium

While deriving the criterion for spontaneity of a process at constant temperature and pressure in terms of Gibbs energy we used Clausius inequality. It implies that we had taken into account both reversible and irreversible processes. Let us now take the reversible and irreversible processes separately. For reversible process, we can write from Eq. (1.13)

$$T\mathrm{d}S = \partial q_{rev} \qquad \ldots(1.13)$$

And as per Eq. (1.32) we have,

$$\mathrm{d}H = \partial q_p \qquad \ldots(1.32)$$

Comparing Eq. (1.13) and Eq. (1.32) we can write,

$$dH = TdS. \text{ or } \quad dH - T\mathrm{d}S = 0. \qquad \ldots(1.39)$$

This implies that, for a reversible process.

$$\mathrm{d}G = 0 \qquad \ldots(1.40)$$

Now, for an irreversible process

$$T\mathrm{d}S > \partial q_{irr}. \qquad \ldots(1.41)$$

Substituting in Eq. (1.37) we get

$$\mathrm{d}G < 0\ . \qquad \ldots(1.42)$$

Since all spontaneous reactions are irreversible, Eq. (1.42) serves as a criteria for spontaneity for a process occurring under constant temperature and constant pressure conditions.

**Relation between Spontaneity, Gibbs Energy and Entropy of Universe**

You would recall that according to the second law of thermodynamics, the entropy change for an isolated system is equal to or greater than zero for a spontaneous process. That is,

$$\mathrm{d}S \geq 0 \qquad \ldots(1.43)$$

In an isolated system, $\mathrm{d}S = 0$ for a reversible process, and $\mathrm{d}S \geq 0$ for an irreversible process. We know that generally a system interacts primarily with its immediate surroundings. Thus, the system and its immediate surroundings can be assumed to be isolated from the rest of the universe. Such a system is said to be a **composite isolated system** and the total entropy of such a systemis given by the expression

$$\mathrm{d}S_{total} = \mathrm{d}S_{system} + dS_{surroundings} \qquad \ldots(1.44)$$

Since the surroundings are much larger than the system, the gain or loss of energy as heat by the surroundings is taken as reversible process irrespective of whether the process is reversible or not. Therefore, we can write,

$$\mathrm{d}S_{surroundings} = \frac{\partial q_{surroundings}}{T} = -\frac{\partial q_{system}}{T} \qquad \ldots(1.45)$$

We know that at constant pressure, $\partial q_{system} = \mathrm{d}H_{system}$

Therefore, we can write Eq. (1.44) as

$$\mathrm{d}S_{total} = \mathrm{d}S_{system} - \frac{dH_{system}}{T} \qquad \ldots(1.46)$$

Simplifying,

$$\mathrm{d}S_{total} = -\frac{T\mathrm{d}S_{system} - dH_{system}}{T} \qquad \ldots(1.47)$$

$$\mathrm{d}S_{total} = -\frac{\mathrm{d}G_{system}}{T} \qquad \ldots(1.48)$$

Since, d$S_{total}$ increases for a spontaneous irreversible process, therefore, for a spontaneous process at constant temperature and pressure, we can say that

$$-\frac{\mathrm{d}G_{system}}{\mathrm{T}} > 0. \text{ or } \mathrm{d}G_{system} < 0 \qquad \ldots(1.49)$$

It is important to note that ΔG depends only on the initial and final states ofthe system. It does not provide any information about the rate or the kinetics of the process.

*This is the desired criteria for the spontaneity of a process under constant temperature and pressure conditions.* According to it, for a spontaneous process, Gibbs energy decreases and Gibbs energy change for the system is negative. Thus, we can predict the spontaneity of a process based on the thermodynamic properties of the system. For a finite change, the criterion for spontaneity of a process at constant temperature and pressure is given as

$$(\Delta G)_{T,p} < 0. \qquad \ldots(1.50)$$

If the Gibbs energy decreases for a spontaneous process, it implies that for a non-spontaneous process the Gibbs energy will increase. If the change in Gibb energy (d$G$) is negative for the process in the forward direction, then d$G$ will be positive for the process in the backward direction. At equilibrium,

$$(\Delta G)_{T,p} = 0. \qquad \ldots(1.51)$$

Using Eq. (1.35) we can say that both d$H$ and Td$S$ contribute to the spontaneity of a process. For a finite change at constant temperature and pressure, the change in Gibbs energy is written as

$$(\Delta G)_{T,p} = \Delta H - T\Delta S. \qquad \ldots(1.52)$$

There are different combinations of enthalpy change and entropy change possible for different processes. As discussed in case of Helmholtz energy, we can consider different cases and see whether and under what conditions the process will be spontaneous for each such combination. The conditions for spontaneity and equilibrium for different combinations of Δ$H$ and Δ$S$ are compiled in Table 1.2

**Table 1.2: The conditions for spontaneity and equilibrium for different combinations of $\Delta H$ and $\Delta S$.**

| S. No. | Combination of $\Delta H$and $\Delta S$ | Condition for spontaneity | Condition for equilibrium | Remark |
|---|---|---|---|---|
| 1 | $\Delta H < 0$ and $\Delta S > 0$ | $\Delta H - T\Delta S < 0$ | $\Delta G = 0$ | Spontaneous at all temperatures; equilibrium not observed |
| 2 | $\Delta H > 0$ and $\Delta S < 0$ | $\Delta H - T\Delta S < 0$ | $\Delta G = 0$ | Nonspontaneous at all temperatures; equilibrium not observed |
| 3 | $\Delta H < 0$ and $\Delta S < 0$ | $\lvert\Delta H\rvert > \lvert T\Delta S\rvert$ | $\lvert T\Delta S\rvert = \lvert\Delta H\rvert$ | Equilibrium at $T = \lvert\Delta H\rvert / \lvert\Delta S\rvert$<br>Spontaneous at temperatures lower than the equilibrium temperature |
| 4 | $\Delta H > 0$ and $\Delta S > 0$ | $\lvert\Delta H\rvert < \lvert T\Delta S\rvert$ | $\lvert T\Delta S\rvert = \lvert\Delta H\rvert$ | Equilibrium at $T = \lvert\Delta H\rvert / \lvert\Delta S\rvert$<br>Spontaneous at temperatures higher than the equilibrium temperature |
| 5 | $\Delta S = 0$ | $\lvert\Delta H\rvert < 0$ | $\Delta H = 0$ | Spontaneous only for exothermic processes |
| 6 | $\Delta H = 0$ | $\lvert\Delta S\rvert > 0$ | $\Delta S = 0$ | The entropy must increase for the process to be spontaneous |

Let us take an example to see how we can predict the spontaneity of a process by computing its Gibbs energy change.

**Example 1.2:** For a system undergoing isothermal and isobaric process, the changes in enthalpy and entropy were found to be 58 kJ mol$^{-1}$ and 185 J K$^{-1}$mol$^{-1}$, respectively.

a) Will the process be spontaneous at 330K?

b) Calculate the temperature at which the system will attain equilibrium assuming that the enthalpy and entropy changes are not affected by the change in temperature.

**Solution:** a) For the process to be spontaneous ΔG must be negative. We know that $(\Delta G)_{T,p} = \Delta H - T\Delta S$

Given: $\Delta H = 58\,\text{kJ mol}^{-1} = 58000\,\text{J mol}^{-1}$

$\Delta S = 185\,\text{JK}^{-1}\,\text{mol}^{-1}$ and $T = 330$ K

Substituting the values, we get

$$58000\,\text{J mol}^{-1} - (330\,\text{K} \times 185\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= 58000 - 61050\,\text{J mol}^{-1} = -3050\,\text{J mol}^{-1}$$

Since the computed value of the Gibbs energy change is negative, the process will be spontaneous.

b) The system will attain equilibrium when $|\Delta H| = |T\Delta S|$

Since the temperature is constant, we can write

$$T = \frac{|\Delta H|}{|\Delta S|}$$

Substituting the values

$$T = \frac{|\Delta H|}{|\Delta S|} == \frac{58000\ \text{J mol}^{-1}}{185\ \text{JK}^{-1}\ \text{mol}^{-1}} = 313.51\text{K}$$

Thus, the system will attain equilibrium at 313.51 K.

Having learnt about the criterion for spontaneity of the processes occurring under constant temperature and constant pressure conditions in terms of Gibbs energy let us now see the physical significance of Gibbs energy.

### 1.3.2 Physical Significance of Gibbs Energy

Let us start with the expression for Gibbs energy, $G = H - TS$ and substituting for enthalpy, $H = U + pV$ we can write

$$G = U + pV - TS \qquad \ldots(1.53)$$

The change in Gibbs energy can then be written as

$$\text{d}G = \text{d}U + p\text{d}V + V\text{d}p - T\text{d}S - S\text{d}T \qquad \ldots(1.54)$$

You would recall from above that by combining the expressions for the first and second law we can write

$$\text{d}U = T\text{d}S + \partial w_{rev} \qquad \ldots(1.29)$$

Substituting the expression for d$U$ in Eq. (1.54) and simplifying we get,

$$\begin{aligned} dG &= +T\text{d}S + \partial w_{rev} + p\text{dV} + \text{Vd}p - T\text{d}S - S\text{d}T \\ dG &= \partial w_{rev} + p\text{dV} + \text{Vd}p - S\text{d}T \end{aligned} \qquad \ldots(1.55)$$

As the change in Gibbs energy is equal to the energy that is available with the system to do useful work, Gibbs energy was earlier known as free energy or Gibbs free energy.

- The decrease in Gibbs energy is equal to the maximum amount of useful work (i.e., non-expansion work) that can be obtained from a system undergoing a reversible process under constant temperature and pressure conditions.
- The increase in free energy of the system is equal to the work done on the system over and above the mechanical work.

At constant temperature and constant pressure, i.e., d$T$ = 0 and d$p$ = 0, the Eq. (1.55) becomes

$$\text{d}G = \partial w_{rev} + p\text{d}V \qquad \ldots(1.56)$$

$\partial w_{rev}$ is the total work done on the system under reversible conditions at constant temperature and pressure. This can include all types of work like electrical work, chemical work, or mechanical work. You know that the mechanical work is the work of expansion or compression and is given by the following expression,

$$\partial w_{mechnical} = -p\text{d}V \qquad \ldots(1.57)$$

Substituting in Eq. (1.56) we get

$$\text{d}G = \partial w_{rev} - \partial w_{mechanical} \qquad \ldots(1.58)$$

Here, $\partial w_{rev} - \partial w_{mechnical}$ is the non-expansion work. We can call it the net work done under reversible condition and write.

$$dG = \partial w_{rev} - \partial w_{mechanical} = \partial w_{net,rev} \qquad \ldots(1.59)$$

As you know that the work done by the system is ($-\partial w$), therefore,

$$-dG = (-\partial w_{net,rev}) \qquad \ldots(1.60)$$

Recall that the system does maximum work under reversible conditions, i.e., $|\partial w_{net,rev}|$ is the maximum amount of work that a system can do. Therefore, we can say that *the decrease in Gibbs energy is equal to the maximum amount of useful work(i.e., non-expansion work) that can be obtained from a system undergoing a reversible process under constant temperature and pressure conditions.*

## 1.4.1 Relation between Gibbs Energy and Helmholtz Energy

Starting with Eq. (1.36) and the relation between enthalpy and internal energy $H = U + pV$, we can write

$$G = H - TS = U + pV - TS \qquad \ldots(1.53)$$

We know from Eq. (1.21), that $A = U - TS$. Substituting in Eq. (1.53), we get

$$G = A + pV \qquad \ldots(1.61)$$

Let the initial state of the system be $G_1$, $A_1$, $p_1$, $V_1$and $T_1$ and the final state of the system be$G_2$, $A_2$, $p_2$, $V_2$and $T_2$. We can write

$$G_1 = A_1 + p_1V_1 \text{ and } G_2 = A_2 + p_2V_2 \qquad \ldots(1.62)$$

The change in Gibbs energy can be given by the following expression

$$G_2 - G_1 = (A_2 - A_1) + (p_2V_2 - p_1V_1)$$

$$\Delta G = \Delta A + (p_2V_2 - p_1V_1) \qquad \ldots(1.63)$$

You know that for an ideal gas

$$p_2V_2 = nRT_2 \text{ and } p_1V_1 = nRT_1 \qquad \ldots(1.64)$$

Therefore, by substituting the above expressions, Eq. (1.63) can be modified for an ideal gas as

$$\Delta G = \Delta A + nR(T_2 - T_1) \qquad \ldots(1.65)$$

If the temperature is kept constant during the changei.e.,$T_2 = T_1$. We get

$$\Delta G = \Delta A \qquad \ldots(1.66)$$

For an isothermal process involving an ideal gas, the change in Gibbs energy and change in Helmholtz energy are equal.

Thus, for an isothermal pressure-volume change process involving an ideal gas, the change in Gibbs energy and change in Helmholtz energy are equal.

Having learnt about the Helmholtz and Gibbs energy and their physical significance and interrelationship we will take up the properties of Helmholtz energy and Gibbs energy. However, before that try to solve following simple questions to assess your understanding.

## SAQ 1

Predict whether the process will be spontaneous or non-spontaneous for the following cases at 300 K:

(i) $\Delta U = 35\,\text{kJ mol}^{-1}$ and $\Delta S = 180\,\text{J K}^{-1}\text{mol}^{-1}$

(ii) $\Delta U = 15.6\,\text{kJ mol}^{-1}$ and $\Delta S = -210\,\text{J K}^{-1}\text{mol}^{-1}$

(iii) $\Delta U = 78.5\,\text{kJ mol}^{-1}$ and $\Delta S = 80.5\,\text{J K}^{-1}\text{mol}^{-1}$

## SAQ 2

The change in internal energy for a system undergoing isothermal process at constant volume was found to be 25 kJmol$^{-1}$ and the entropy change was found to be 90 J K$^{-1}$mol$^{-1}$.Calculate the temperature at which the system will attain equilibrium assuming that the internal energy change and entropy change do not vary with temperature.

## SAQ 3

Based on the given values of $\Delta H$ and $\Delta S$ predict which one of the following processes will be spontaneous at 300 K?

(i) $\Delta H = -2.5\,\text{kJ mol}^{-1}$ and $\Delta S = 150\,\text{J K}^{-1}\text{mol}^{-1}$

(ii) $\Delta H = 18\,\text{kJ mol}^{-1}$ and $\Delta S = -25\,\text{J K}^{-1}\text{mol}^{-1}$

(iii) $\Delta H = 18\,\text{kJ mol}^{-1}$ and $\Delta S = 0\,\text{J K}^{-1}\text{mol}^{-1}$

(iv) $\Delta H = 0\,\text{kJ mol}^{-1}$ and $\Delta S = 25\,\text{J K}^{-1}\text{mol}^{-1}$

# 1.4 PROPERTIES OF GIBBS ENERGY AND HELMHOLTZ ENERGY

In previous section you have studied the importance of Gibbs energy change and Helmholtz energy change in predicting spontaneity and equilibrium when certain parameters were kept constant. In this section we will further elaborate their properties which can be used for calculating various thermodynamic properties of the system. We begin with the temperature and pressure dependence of Gibbs energy.

## 1.4.2 Temperature and Pressure Dependence of Gibbs Energy

In the process of deriving the expressions for Gibbs energy we have considered the temperature and pressure to be constant. This implies that while the process is taking place, we do not change the temperature and pressure of the system. However, the process can be carried out at different sets of temperatures and pressures. The question is what will be the effect of performing the process at a different temperature (s) or pressure (s). Further, you may know that the standard tables of thermodynamic data on Gibbs energy, enthalpy or entropy are compiled for the standard state. If we have a system at a temperature different from standard state then we need to consider the temperature dependence of G and get the required data.

In other words, how does the Gibbs energy of the system change on changing the temperature or pressure. Here we will consider two possibilities viz.,

i. Variation of Gibbs energy with temperature at constant pressure, and

ii. Variation of Gibbs energy with pressure at constant temperature,

Let us consider a system undergoing reversible *p-V* change. Using Eq. (1.53) we can write,

$$G = U + pV - TS \qquad \text{…(1.53)}$$

The change in Gibbs energy is given by the expression

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T \qquad \text{…(1.54)}$$

For a reversible *p-V* change, we can write from Eq. (1.14)

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \qquad \text{…(1.14)}$$

Substituting in Eq. (1.54) and simplifying the expression*,* we get

$$\mathrm{d}G = T\mathrm{d}S - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - SdT$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \qquad \text{…(1.67)}$$

Thus, we can say that for a system undergoing reversible *p-V* change the Gibbs energy change depends upon temperature and pressure. This can be mathematically expressed as

$$G = f(T, p) \qquad \text{…(1.68)}$$

The change in Gibbs energy in terms of change in temperature and pressure can be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \qquad \text{…(1.69)}$$

The derivative in first term on the right of Eq. (1.69)gives the rate of change of Gibbs energy with temperature at constant pressure and dT is the total change in the temperature. Similarly, the derivative in second term on right gives the rate of change of Gibbs energy with pressure at constant temperature and dp is the total change in the pressure. Comparing Eqs. (1.67) and (1.69) in terms of coefficients of d*T* and d*p* we get

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \text{ and } \left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{…(1.70)}$$

This implies that the rate of change of Gibbs energy with temperature at constant pressure equals the decrease in the entropy. Also, the rate of change of Gibbs energy with pressure at constant temperature equals increase in the volume.

Let us now take up the variation of Gibbs energy with temperature at constant pressure.

### i. Variation of Gibbs energy with temperature at constant pressure: Gibbs-Helmholtz equation

The Eq.(1.69) gives the total change in the Gibbs energy when the temperature and pressure change by dT and dp respectively. However, it is always easier to study the variation of thermodynamic property with change in any one parameter, keeping the rest of the parameters constant. Therefore, while studying the changes in Gibbs energy due to change in temperature and pressure, we keep one variable constant and change the second variable. According to Eq. (1.67), at constant pressure, we can write

$$(\mathrm{d}G)_p = -S\mathrm{d}T \qquad \ldots(1.71)$$

Now, to find the total change in Gibbs energy with the change in temperature we have to integrate the above expression. That is,

$$\int_{G_1}^{G_2} \mathrm{d}G = -\int_{T_1}^{T_2} S\mathrm{d}T \qquad \ldots(1.72)$$

As the entropy is temperature dependent, it is taken inside the integral. Integrating the above expression, we get

$$G_2 - G_1 = -\int_{T_1}^{T_2} S\mathrm{d}T \qquad \ldots(1.73)$$

Since the entropy increases with the increase in temperature, the right-hand side of the above expression will be less than zero. *Therefore, we can say that Gibbs energy decreases with the increase in temperature.*

Using Eq. (1.36) and Eq. (1.70) we can write

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p \qquad \ldots(1.74)$$

Rearranging, we get

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p \qquad \ldots(1.75)$$

Dividing Eq. (1.75) throughout by $T^2$we get

$$\frac{H}{T^2} = \frac{G - T\left(\frac{\partial G}{\partial T}\right)_p}{T^2} \qquad \ldots(1.76)$$

To simplify the above expression, we take a function *G/T* and differentiate it with respect to *T* at constant *p*. This gives

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{T\left(\frac{\partial G}{\partial T}\right)_p - G}{T^2} \qquad \ldots(1.77)$$

Comparing Eqs. (1.76) and (1.77) we get

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2} \qquad \text{…(1.78)}$$

The Eq. (1.78) is known as **Gibbs-Helmholtz equation.** According to Gibbs-Helmholtz equation, if the enthalpy of the system is known, we can calculate the variation of *G/T* with the change in temperature. This relation is very useful while studying chemical equilibrium.

### ii. Variation of Gibbs energy with pressure at constant temperature

According to Eq. (1.70), the change in Gibbs energy with pressure at constant temperature is given by the following expression

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{…(1.70)}$$

Therefore, we can write

$$(\mathrm{d}G)_\mathrm{T} = V\mathrm{d}p \qquad \text{…(1.79)}$$

To find the total change in Gibbs energy with the change in pressure we need to integrate the above expression. That is,

$$\int_{G_1}^{G_2} \mathrm{d}G = \int_{p_1}^{p_2} V\mathrm{d}p \qquad \text{…(1.80)}$$

Since the volume varies with the change in pressure, it is taken inside the integral. However, for solids and liquids, we can assume that the volume is constant for small changes in pressure. Therefore, on integration we get,

$$G_2 - G_1 = V(p_2 - p_1) \qquad \text{…(1.81)}$$

From this expression we can conclude that for solids and liquids there is an increase in Gibbs energy with the increase in pressure. On the other hand, in case of gases we cannot assume that the volume is constant. So, we need to use a relation between volume and pressure of the gas. Assuming that the gas behaves ideally, we can write

$$V = \frac{nRT}{p} \qquad \text{…(1.82)}$$

Substituting in Eq. (1.80) and integrating within limits, we get

$$G_2 - G_1 = \int_{p_1}^{p_2} \frac{nRT}{p}\mathrm{d}p = nRT\ln\frac{p_2}{p_1} \qquad \text{…(1.83)}$$

As the pressure is increased, $(p_2 > p_1)$ the right-hand side of the above equation will be greater than zero. Hence, for ideal gas, the Gibbs energy increases with the increase in pressure. We know that for an ideal gas under isothermal condition, $p_2V_2 = p_1V_1$.

Substituting in Eq. (1.83), we get

$$\Delta G = G_2 - G_1 = nRT\ln\frac{V_1}{V_2} \qquad \text{…(1.84)}$$

Eq. (1.84) can be used to calculate the Gibbs energy change during isothermal reversible expansion or compression of an ideal gas. Let us take an example to understand it.

**Example 1.3:** One mole of an ideal gas undergoes isothermal expansion from 10 L to 100 L at 300 K. Calculate the change in Gibbs energy for the process.

**Solution:** As per Eq. (1.84)

$$\Delta G = nRT \ln \frac{V_1}{V_2} = 2.303\, nRT \log \frac{V_1}{V_2}$$

**Given**: $n = 1\,\text{mol},\ R = 8.314\,\text{JK}^{-1}\text{mol}^{-1}, T = 300\text{K}, V_1 = 10\,L, V_2 = 100\,\text{L}$

Substituting the values,

$$\Delta G = 2.303 \times 1\text{mol} \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 300\,\text{K} \times \log \frac{10}{100}$$

$$\Delta G = -5744.14\,\text{J}$$

Thus, the change in Gibbs energy for the process will be

$$\Delta G = -5744.14\,\text{J} \ \text{ or } \ -5.744\,\text{kJ}$$

Having learnt about the temperature and pressure dependence of Gibbs energy let us now take up the temperature and volume dependence of Helmholtz energy. However, before that answer the following simple questions to assess your understanding.

## *SAQ 4*

Two moles of an ideal gas are compressed isothermally at 298 K from 2.5 bar to 1 bar. Calculate the change in Gibbs energy and change in molar Gibbs energy.

## *SAQ 5*

The Gibbs energy of one mole of an ideal gas at 300 K and 1 bar is $-3.6\ \text{kJmol}^{-1}$. Calculate the Gibbs energy of this gas at 298 K and 2 bar.

### 1.4.3 Temperature and Volume Dependence of Helmholtz Energy

In the process of deriving the expressions for Helmholtz energy we have considered the temperature and volume to be constant. This implies that while the process is taking place, we do not change the temperature and volume of the system. However, the process can be carried out at different sets of temperatures and volumes. The question is what will be the effect of performing the process at a different temperature (s) or volume (s). In other words, how does the Helmholtz energy of the system change on changing the temperature and volume. Here we will consider two possibilities viz.,

i. Variation of Helmholtz energy with temperature at constant volume, and

ii. Variation of Helmholtz energy with volume at constant temperature,

Let us start with Eq. (1.21)

$$A = U - TS \qquad \text{…(1.21)}$$

The change in Helmholtz energy can be expressed as

$$\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \qquad \text{…(1.85)}$$

Since for a reversible *p-V* change, we can write from Eq. (1.14)

$$\mathrm{dU} = T\mathrm{d}S - p\mathrm{dV} \qquad \text{…(1.14)}$$

Substituting in Eq. (1.85) and simplifying, we get

$$\mathrm{dA} = T\mathrm{d}S - p\mathrm{dV} - T\mathrm{d}S - SdT$$

$$\mathrm{dA} = -S\mathrm{d}T - p\mathrm{dV} \qquad \text{…(1.86)}$$

Thus, we can say that for a system undergoing reversible *p-V* change the Helmholtz energy depends upon temperature and volume. This can be mathematically expressed as

$$A = f(T,V) \qquad \text{…(1.87)}$$

The change in Helmholtz energy with the change in temperature and volume is given as

$$\mathrm{d}A = \left(\frac{\partial A}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial A}{\partial V}\right)_T \mathrm{d}V \qquad \text{…(1.88)}$$

In this expression Eq. (1.88), the derivative in first term on the right gives the rate of change of Helmholtz energy with temperature at constant volume and dT is the total change in the temperature. Similarly, the derivative in second term gives the rate of change of Helmholtz energy with volume at constant temperature and d*V* is the total change in the volume. Comparing the coefficients of d*T* and d*V* in Eqs. (1.86) and (1.88) we get

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \text{…(1.89)}$$

This implies that the rate of change of Helmholtz energy with temperature at constant volume equals the decrease in the entropy and the rate of change of Helmholtz energy with volume at constant temperature equals the decrease in the pressure.

Let us now take up the variation of Helmholtz energy with temperature at constant volume.

### i. Variation of Helmholtz energy with temperature at constant volume: Gibbs-Helmholtz equation

The Eq.(1.88) gives the total change in the Helmholtz energy when the temperature and volume change by d*T* and d*V* respectively. However, it is always easier to study the variation of thermodynamic property with change in any one parameter, keeping all other parameters constant. Therefore, while studying the changes in Helmholtz energy due to change in temperature and volume, we keep one variable constant and change the second variable. According to Eq. (1.86), at constant volume, we can write

$$(\mathrm{d}A)_v = -S\mathrm{d}T \qquad \text{…(1.86)}$$

To find the total change in Helmholtz energy with the change in temperature we need to integrate the above expression. That is,

$$\int_{A_1}^{A_2} \mathrm{d}A = -\int_{T_1}^{T_2} S\mathrm{d}T \qquad \text{…(1.90)}$$

The entropyis taken inside the integral as it is temperature dependent. Integrating the left side of the equation and applying limits, we get

$$\Delta A = A_2 - A_1 = -\int_{T_1}^{T_2} S\mathrm{d}T \qquad \text{…(1.91)}$$

Since absolute entropy is always greater than zero, this implies that Helmholtz energy decreases with the increase in temperature at constant volume.

The variation of Helmholtz energy with temperature can be used to derive another form of Gibbs-Helmholtz equation. Starting from Eq. (1.21) and using Eq. (1.89), we can write

$$A = U + T\left(\frac{\partial A}{\partial T}\right)_V \qquad \text{…(1.92)}$$

Rearranging the equation, we get

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_V \qquad \text{…(1.93)}$$

Dividing Eq. (1.93) throughout by $T^2$ we get

$$\frac{U}{T^2} = \frac{A - T\left(\frac{\partial A}{\partial T}\right)_V}{T^2} \qquad \text{…(1.94)}$$

To simplify the above expression, we take a function *A/T* and differentiate it with respect to *T* at constant *V*. This gives

$$\left[\frac{\partial\left(A/T\right)}{\partial T}\right]_V = \frac{T\left(\frac{\partial A}{\partial T}\right)_V - A}{T^2} \qquad \text{…(1.95)}$$

Comparing the above expression with Eq. (1.94), we get

$$\left[\frac{\partial\left(A/T\right)}{\partial T}\right]_V = -\frac{U}{T^2} \qquad \text{…(1.96)}$$

Eq. (1.96) is the **Gibbs-Helmholtz equation** in terms of Helmholtz energy. According to this form of Gibbs-Helmholtz equation, if the internal energy of the system is known, we can calculate the variation of *A/T* with the change in the temperature.

### ii. Variation of Helmholtz energy with volume at constant temperature

To understand the variation of Helmholtz energy with volume at constant temperature we start with the following expression obtained from Eq. (1.86), under constant temperature conditions,

$$(\mathrm{d}A)_\mathrm{T} = -p\mathrm{dV} \qquad \ldots(1.97)$$

To find the total change in Helmholtz energy with the change in volume at constant temperature we need to integrate the above expression. That is

$$\int_{A_1}^{A_2} \mathrm{d}A = -\int_{V_1}^{V_2} p\mathrm{d}V \qquad \ldots(1.98)$$

We know that for an ideal gas $p = \frac{nRT}{V}$. Substituting in Eq. (1.98) and integrating we get

$$A_2 - A_1 = -nRT\int_{V_1}^{V_2} \frac{1}{V}dV = -nRT\ln\frac{V_2}{V_1}$$

$$\text{or} \qquad \Delta A = nRT\ln\frac{V_1}{V_2} \qquad \ldots(1.99)$$

In terms of pressure, Eq. (1.99) can be written as

$$A_2 - A_1 = nRT\ln\frac{p_2}{p_1} \qquad \ldots(1.100)$$

According to Eq. (1.100), during the expansion of an ideal gas under isothermal conditions, the Helmholtz energy of the system decreases. It is interesting to note that the expressions for the change in Gibbs energy for an isothermal expansion of an ideal gas (Eq. (1.67)) and the one for the change in Helmholtz energy for isothermal expansion (Eq. (1.99)) are identical. This can be rationalised in terms of Eq. (1.66) where we showed that the change in Gibbs energy and Helmholtz energy for an isothermal process are equal. Let us take the data of Example 3 discussed above and calculate the change in Helmholtz energy for the process.

**Example 1.4:** One mole of an ideal gas undergoes isothermal expansion from 10 L to 100 L at 300 K. Calculate the change in Helmholtz energy for the process.

**Solution:** As per Eq. (1.99)

$$\Delta A = 2.303\, nRT\log\frac{V_1}{V_2}$$

Given: $n = 1\,\text{mol},\ R = 8.314\,\text{JK}^{-1}\,\text{mol}^{-1}, T = 300\text{K}, V_1 = 10\,L, V_2 = 100\,\text{L}$

Substituting the values in the above equation we get

$$\Delta A = 2.303 \times 1 mol \times 8.314\,\text{JK}^{-1}\,\text{mol}^{-1} \times 300\,\text{K} \times \log\frac{10}{100}$$

$$\Delta A = -5744.14\,\text{J}$$

Thus, the change in Helmholtz energy for the process will be

$$\Delta G = -5744.14\,\text{J} \text{ or } -5.744\,\text{kJ mol}^{-1}$$

## 1.4.4 Maxwell's Relations

We have so far defined four different state functions viz., *U*, *H*, *A*, and *G*. Each one of these has dimensions of energy. A question comes up is that in what way are these different? You would recall that internal energy (*U*) represents the sum of the kinetic and potential energies of all the components of the system. On the other hand, the enthalpy, *H* equals the heat flows into or out of the system for a thermodynamic process carried out under constant pressure conditions. Further, as discussed above, the Helmholtz energy *A* represents the *maximum total work* that can be produced in a process whereas, the Gibbs energy *G* gives the *maximum non-expansion work* that the process can produce. In addition, the change in Helmholtz energy and change in Gibbs energy provide criteria for the spontaneity of a process under constant T & V and constant *T*&*p* conditions respectively.

We know that the macroscopic variables i.e., *T* (temperature),*p* (pressure), V (volume) and m (mass) of the system can be measured directly. Further, some properties like, density and specific volume can be determined easily by using these. On the other hand, the properties like internal energy, enthalpy, and entropy cannot be measured directly or determined by using the above properties. It is, therefore, desirable that we develop some fundamental relations between the thermodynamic properties that cannot be measured directly in terms of easily measurable properties.

Therefore, the next issue we take up is to develop the relations for the dependence of state functions on the macroscopic variables i.e., *T* (temperature), *S* (entropy), *p* (pressure), and V (volume) of the system. For a simple compressible system, the state functions are related to the derivatives of properties *p, V, T* and *S* with respect to each other. These are very important relations and are known as **Maxwell's relations or Maxwell's equations**. These can be derived from the expressions corresponding to the exact differentials of the state functions. Let us first work out these expressions.

We begin by recalling Eq. (1.14)

$$\text{d}U = T\,\text{dS} - p\text{d}V \qquad \ldots(1.14)$$

As mentioned above, this equation is referred to as the **fundamental equation of thermodynamics** and represents the exact differential of the state function *U*. We can use this expression to workout similar expressions for the exact or total differentials of the other state functions. We begin with enthalpy and recallits definition, i.e.,

$$H = U + pV \qquad \ldots(1.101)$$

Differentiating it, we get

$$dH = dU + pdV + VdP \qquad \ldots(1.102)$$

Substituting Eq. (1.14) into Eq. (1.102), we get

$$dH = TdS - pdV + pdV + Vdp \qquad \ldots(1.103)$$

Simplifying, we get the desired expression as

$$dH = T\,dS + V\,dp. \qquad \ldots(1.104)$$

Again, for Helmholtz energy we begin with the definition of Helmholtz energy, i.e.,

$$A = U - TS \qquad \ldots(1.21)$$

Differentiating it, we get

$$dA = dU - TdS - SdT \qquad \ldots(1.105)$$

Substituting Eq. (1.14) into Eq. (1.105), gives

$$dA = TdS - pdV - TdS - SdT \qquad \ldots(1.106)$$

Simplifying, we get the desired expression as

$$dA = -pdV - SdT \qquad \ldots(1.107)$$

Similarly, for Gibbs energy the desired expression can be determined to be

$$dG = VdP - SdT \qquad \ldots(1.108)$$

The expressions [(1.14), (1.104)(1.107)and (1.108)] derived above represent the exact differentials of the state functions. Sometimes these are called **the Gibbs equations.** These show how the dependent variable on the left side varies as a function of changes in two independent variables on the right side. For example, *U* is dependent on *S* and *V*. These independent variables are the natural variables of the corresponding dependent variable. The state functions and the corresponding exact differentials are compiled in Table 1.1,along with the thermodynamic functions indicating the independent variables of these state functions.

**Table 1.1: The state functions, expression (fundamental equations) for their exact differentials and the corresponding thermodynamic functions**

| State Function | The expression or fundamental equations for exact differentials | Thermodynamic function |
|---|---|---|
| $U$ | $dU = TdS - pdV$ | $U = f(S,V)$ |
| $H$ | $dH = TdS + Vdp$ | $H = f(S,p)$ |
| $A$ | $dA = -pdV - SdT$ | $A = f(V,T)$ |
| $G$ | $dG = Vdp - SdT$ | $G = f(p,T)$ |

There are two important aspects of these fundamental equation:

- Each of these fundamental equations is equally basic and is always valid. In a way, these give four equivalent ways of conveying the same information. The choice to use them depends on the set of independent variables $(S,V)$, $(S,p)$, $(T,V)$, or $(T,p)$ appropriate for a given system.

- The fundamental equations are derived assuming a reversible process. However, since these represent total differentials, these apply equally to the irreversible processes also.

We are now equipped to derive the Maxwell relations. As stated above, these give the variation of one thermodynamic property with respect to the other thermodynamic property under certain conditions. Starting with the combined form of first and second laws of thermodynamics for a reversible $p$-$V$ change, we can write

$$dU = T\mathrm{d}S - pdV \qquad \text{...(1.14)}$$

Differentiating Eq. (1.14) with respect to $S$at constant $V$ we get

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{…(1.109)}$$

Differentiating Eq. (1.109) with respect to $V$ at constant $S$ we get

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial T}{\partial V}\right)_S \qquad \text{…(1.110)}$$

Similarly, differentiating Eq. (1.14) with respect to $V$ at constant $S$ we get

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \text{…(1.111)}$$

Differentiating with respect to $S$ at constant $V$ we get

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_S\right)_V = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \text{…(1.112)}$$

Since $U$ is a state function, Euler's reciprocity relation is valid. Therefore,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \text{...(1.113)}$$

Eq. (1.13) is the first Maxwell relation. For deriving the second Maxwell relation, we start with the Gibbs equation related to enthalpy, i.e.,

$$dH = TdS + Vdp \qquad \text{...(1.104)}$$

Differentiating with respect to$p$ at constant $S$ we get

$$\left(\frac{\partial H}{\partial p}\right)_S = V \qquad \text{…(1.114)}$$

Differentiating the above equation with respect to $S$ at constant $p$ we get

$$\left(\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right)_p = \left(\frac{\partial V}{\partial S}\right)_p \qquad \text{…(1.115)}$$

Similarly, differentiating Eq. (1.104)with respect to $S$ at constant $p$ we get

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad \text{…(1.116)}$$

Differentiating the above equation with respect to $p$ at constant $S$ we get

$$\left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right)_S = \left(\frac{\partial T}{\partial p}\right)_S \qquad \text{…(1.117)}$$

Since $H$ is a state function, using Euler's reciprocity relation we can write,

$$\left(\frac{\partial V}{\partial S}\right)_p = -\left(\frac{\partial T}{\partial p}\right)_S \qquad \text{...(1.118)}$$

Eq. (1.118) is the second Maxwell relation. Similarly, we can derive Maxwell relations by starting with the Gibbs equations related to Gibbs energy, and Helmholtz energy respectively i.e.,

$$dA = -PdV - SdT \qquad \text{…(1.107)}$$

$$dG = -SdT + Vdp \qquad \text{…(1.108)}$$

The Maxwell relations so obtained are,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \text{…(1.119)}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \qquad \text{…(1.120)}$$

***Significance of Maxwell Relations***

As stated above, Maxwell equations relate the state functions to the derivatives of properties $p$, $V$, $T$ and $S$ with respect to each other. Therefore, these can be used to calculate the variations in those properties which cannot be measured directly through experiments. For example, the variation of entropy with volume cannot be determined experimentally. However, variation of pressure with temperature at constant volume can be experimentally studied. Therefore, $(\partial S/\partial V)_T$ can be calculated with the help of Eq. (1.119). Similarly, the variation of entropy with pressure can be determined with the help of Eq. (1.120) by studying the variation of volume with temperature at a constant pressure.

Having learnt about Maxwell relations, let us discuss about the Gibbs energy change for a reaction. However, before that answer the following simple question to assess your understanding.

Maxwell relations provide relationships between seemingly unconnected thermodynamic functions.
For example, these can be used to determine the change in entropy by simply measuring the changes in easily measurable properties like p,V and T.

*SAQ 6*

Derive the following expression for Maxwell relation by using Gibbs equation corresponding to Helmholtz function.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

## 1.5 GIBBS ENERGY CHANGE FOR A REACTION

In order to calculate the Gibbs energy for a reaction we assume that at the start of the reaction only the reactants are present in their respective standard states and when the reaction is complete, only products are present in their respective standard states. It is also assumed that the temperature and the pressure remain constant during the reaction. Under these conditions the standard Gibbs energy change for the reaction can be calculated in terms of the Gibbs energy of formation of all the reactants and the products. Standard Gibbs energy of formation of a compound $(\Delta G_f^{\varphi})$ is defined as the Gibbs energy change taking place during the formation of a compound in its standard state from its constituent elements in their respective standard states at constant temperature. For each element in its standard state, the Gibbs energy is assigned a zero value. The standard Gibbs energy change for a reaction is represented as, $= \Delta G^{\varphi}$. Mathematically, we can write the following expression for the standard Gibbs energy change for a reaction,

$$\Delta G^{\varphi} = \sum \Delta G_f^{\varphi}(products) - \sum \Delta G_f^{\varphi}(reac\tan ts) \qquad \ldots(1.121)$$

Alternatively, the standard Gibbs energy change of a reaction can also be calculated from the change in standard enthalpy of formation and standard entropy change values of a reaction at a given temperature.

$$\Delta G^{\varphi} = \Delta H^{\varphi} - T\Delta S^{\varphi} \qquad \ldots(1.122)$$

Where, the change in standard enthalpy of formation and standard entropy change values of a reaction are as given below

$$\Delta H^{\varphi} = \sum \Delta H_f^{\varphi}(products) - \sum \Delta H_f^{\varphi}(reactants) \qquad \ldots(1.123)$$

$$\Delta S^{\varphi} = \sum S^{\varphi}(products) - \sum S^{\varphi}(reactants) \qquad \ldots(1.124)$$

Let us take some examples to learn the calculation of standard Gibbs energy change.

**Example 1.5:** Calculate the standard Gibbs energy change for the following reaction at 300 K using the data given below.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

| Substance | $C_6H_{12}O_6(s)$ | $CO_2(g)$ | $H_2O(l)$ | $O_2(g)$ |
|---|---|---|---|---|
| $\Delta G_f^{\varphi}$ (kJ mol$^{-1}$) | –913 | –395 | –237 | 0 |

**Solution:** We know that according to Eq. (1.123) the standard Gibbs energy change for a reaction is given as

$$\Delta G^{\phi} = \sum \Delta G_f^{\phi}(\text{products}) - \sum \Delta G_f^{\phi}(\text{reactants})$$

The standard Gibbs energy change for the formation of reactants can be calculated as

$$= \sum \Delta G_f^{\phi}(\text{reactants}) = (\Delta G_f^{\phi}(C_6H_{12}O_6)) + (6 \times \Delta G_f^{\phi}(O_2))$$
$$= (-913 + (6 \times 0))\,\text{kJ} = -913\,\text{kJmol}^{-1}$$

Similarly, for products the standard Gibbs energy change can be calculated as

$$\sum \Delta G_f^{\phi}(products) = (6 \times \Delta G_f^{\phi}(H_2O)) + (6 \times \Delta G_f^{\phi}(CO_2))$$
$$= ((-237 \times 6) + (-395 \times 6))\,\text{kJ} = -3792\,\text{kJmol}^{-1}$$

Substituting in the Eq. (1.101) we get,

$$\Delta G^{\phi} = -3792\,\text{kJ} - (-913\,\text{kJ}) = -2879\,\text{kJmol}^{-1}$$

Thus, the Gibbs energy change for the given reaction will be, $= -2879\,\text{kJ mol}^{-1}$

**Example 1.5:** Calculate the standard Gibbs energy change for the following reaction at 300 K from the data given in the table below.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Also, predict whether the reaction will be spontaneous under the given conditions.

| **Substance** | **$N_2$** | **$H_2$** | **$NH_3$** |
|---|---|---|---|
| $\Delta H_f^{\phi}$ (kJmol$^{-1}$) | 0 | 0 | -46 |
| $S^{\phi}$(JK$^{-1}$mol$^{-1}$) | 192 | 131 | 193 |

**Solution:** We know that according to Eq. (1.122) the standard Gibbs energy change for a reaction is given as

$$\Delta G^{\varphi} = \Delta H^{\varphi} - T\Delta S^{\varphi}$$

The change in standard enthalpy of formation is given as

$$\Delta H^{\varphi} = \sum \Delta H_f^{\varphi}(products) - \sum \Delta H_f^{\varphi}(reactants)$$

Substituting the values for the standard enthalpy changes for the products and the reactants, we get

$$\Delta H^{\phi} = (2 \times \Delta H_f^{\phi}(NH_3)) - \{\Delta H_f^{\phi}(N_2) + 3 \times \Delta H_f^{\phi}(H_2)\}$$
$$= \{(-46 \times 2) - (0 + (0 \times 3))\}\,\text{kJmol}^{-1} = -92\,\text{kJmol}^{-1}$$

The standard entropy change for the reaction is given as

$$\Delta S^{\varphi} = \sum S^{\varphi}(products) - \sum S^{\varphi}(reactants)$$

Substituting the values for the standard entropies for the products and the reactants, we get

$$\Delta S^{\phi} = 2\times S^{\phi}(NH_3) - \{S^{\phi}(N_2) + 3\times S^{\phi}(H_2)\}$$

$$= \{(2\times 193) - (192 + (3\times 131))\}\,\mathrm{JK^{-1}mol^{-1}}$$

$$= (386 - 585)\,\mathrm{JK^{-1}mol^{-1}} = -199\,\mathrm{JK^{-1}mol^{-1}}$$

Substituting the values of the change in standard enthalpy of formation and standard entropy change of the reaction in the expression for standard Gibbs energy change, we get

$$\Delta G^{\phi} = \{(-92.0k\mathrm{Jmol^{-1}}) - (300\,\mathrm{K}\times -199\,\mathrm{JK^{-1}mol^{-1}})\}$$
$$= -32300\,\mathrm{Jmol^{-1}} = -32.3\,\mathrm{kJmol^{-1}}$$

Since, the standard Gibbs energy change for the reaction is negative, the reaction will be spontaneous.

Let us now sum up what have we learnt in this unit. However, before that answer the following simple question to assess your understanding.

*SAQ 7*

Calculate the standard Gibbs energy change for the following reaction at 300Kfrom the data given in the table below.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

| **Substance** | **$N_2O_5$** | **$NO_2$** | **$O_2$** |
|---|---|---|---|
| $\Delta H_f^{\phi}$ (kJmol$^{-1}$) | 11.3 | 33.2 | 0 |
| $S^{\phi}$(JK$^{-1}$mol$^{-1}$) | 355.7 | 240 | 205.1 |

Also, predict whether the reaction will be spontaneous under the given conditions.

## 1.6 SUMMARY

In this unit we have discussed about the need, significance and properties of two important thermodynamic functions viz., Gibbs energy and Helmholtz energy. These provide criterion for the spontaneity of thermodynamic processes in terms of the properties of the system. We began the unit by discussing the difficulty in using entropy change as a criterion for spontaneity and outlined the need of new functions for predicting the spontaneity based on the properties of the system only.

In this context initially we considered the processes occurring under constant temperature and constant volume conditions and worked out the criterion for their spontaneity in terms of a new function called Helmholtz energy. It was demonstrated that the Helmholtz energy for a process must decrease for such a process to be spontaneous. Also, for equilibrium the value of $\Delta A$ would be zero. Similarly, the criterion called Gibbs energy was worked out for the spontaneity of the processes occurring under constant temperature and constant pressure conditions. Herein, it was shown that the Gibbs energy for a process must decrease for such a process to be spontaneous and remain unaltered for the process to be at equilibrium.

Thereafter, we discussed about the properties of Helmholtz and Gibbs functions. It was shown that both the functions, *A* and *G,* decrease with the increase in temperature. Under isothermal conditions, it was shown that *A* increases with the increase in volume and *G* increases with the increase in pressure. Further, we derived two important versions of Gibbs-Helmholtz relation which could be used to understand the variation of *G/T* and *A/T* with temperature

This was followed by defining the Standard Gibbs energy change for a reaction in terms of the standard Gibbs energies for the reactants and products. It was also shown that the standard Gibbs energy change for a reaction could be expressed in terms of the standard enthalpy change and standard entropy changes. In the end we worked out different Maxwell's relations and discussed their significance.

## 1.6 TERMINAL QUESTIONS

1. Define spontaneity. Under what conditions of

   i) $\Delta U$ and $\Delta S$

   ii) $\Delta H$ and $\Delta S$

   a reaction is always spontaneous.

2. When $\Delta H > 0$ and $\Delta S < 0$ a reaction is never spontaneous. Give reason.

3. What is work function? State the conditions when change in Gibbs energy is equal to work function.

4. Calculate the change in

   i) Helmholtz energy and

   ii) Gibbs energy

   when two moles of an ideal gas are allowed to expand isothermally at 300 K from 5 bar to 1 bar.

5. Derive the following relations using appropriate expressions.

   a. $\left(\frac{\partial A}{\partial T}\right)_V = -S$

   b. $\left(\frac{\partial A}{\partial V}\right)_T = -p$

   c. $\left(\frac{\partial G}{\partial p}\right)_T = V$

   d. $\left(\frac{\partial G}{\partial T}\right)_p = -S$

6. Define standard Gibbs energy change for a reaction.

7. Calculate the standard Gibbs energy change for the following reaction at 300 K using the data provided.

$$N_2O(g) + 3H_2(g) \rightarrow N_2H_4(g) + H_2O(g)$$

| **Substance** | **$N_2O$** | **$H_2$** | **$N_2H_4$** | **$H_2O$** |
|---|---|---|---|---|
| $\Delta H_f^{\phi}(\text{kJ mol}^{-1})$ | 82 | 0 | 50 | -242 |
| $S^{\phi}(\text{J K}^{-1})$ | 220 | 131 | 120 | 189 |

# 1.7 ANSWERS

## Self-Assessment Questions

1. A process is spontaneous if $\Delta U – T\Delta S < 0$.

   (i) $\Delta U = 35\,\text{kJ}$ and $\Delta S = 180\,\text{JK}^{-1}$

   $\Delta U - T\Delta S = 35000\,\text{J} - 300\,\text{K} \times 180\,\text{JK}^{-1} = -19000\,\text{J}.$

   Since the value is negative, the reaction will be spontaneous.

   (ii) $\Delta U = 15.6\,\text{kJ}$ and $\Delta S = -210\,\text{JK}^{-1}$

   $\Delta U - T\Delta S = -15600\,\text{J} - 300\,K \times -210\,\text{JK}^{-1} = 47400\,\text{J}.$

   Since the value is positive, the reaction will be non-spontaneous.

   (iii) $\Delta U = 78.5$ kJ and $\Delta S = -80.5\,\text{JK}^{-1}$

   $\Delta U - T\Delta S = -78500\,\text{J} - 300\,K \times -80.5\,\text{JK}^{-1} = 54350\,\text{J}.$

   Since the value is positive, the reaction will be non-spontaneous.

2. Given: $\Delta U = 25$ kJ, $\Delta S = 90\,\text{JK}^{-1}$

   At equilibrium, $\Delta U = T\,\Delta S$

   $$T = \frac{\Delta U}{\Delta S} = \frac{25000\,\text{J}}{90\,\text{JK}^{-1}} = 277.78\,\text{K}$$

   Thus, the system will be at equilibrium at 277.8 K

3. The process is spontaneous when $\Delta G < 0$i.e, $\Delta H – T\Delta S < 0$

   (i) $\Delta H = -2.5$ kJ, $\Delta S = 150\,\text{JK}^{-1}$

   Since $\Delta H < 0, \Delta S > 0, \Delta G < 0.$ The process is spontaneous

   (ii) $\Delta H = 18$ kJ and $\Delta S = -25\,\text{JK}^{-1}$

   Since $\Delta H < 0, \Delta S > 0, \Delta G > 0.$ The process is non-spontaneous.

   (iii) $\Delta H = 18$ kJ and $\Delta S = 0\,\text{J K}^{-1}$

   Since $\Delta H > 0, \Delta S = 0, \Delta G > 0.$ The process is non-spontaneous.

   (iv) $\Delta H = 0$ kJ and $\Delta S = 25\,\text{J K}^{-1}$

   Since $\Delta H > 0, \Delta S > 0, \Delta G < 0.$ The process is spontaneous.

4. Given: $n = 2\,\text{mol}, T = 298K, p_1 = 2.5\,\text{bar}, p_2 = 1\text{bar}, R = 8.314\,\text{JK}^{-1}\text{mol}^{-1}$

$$\Delta G = 2.303\, nRT \log\frac{p_2}{p_1}$$

$$= 2.303 \times 2\text{mol} \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 298\,\text{K} \times \log\frac{1\text{bar}}{2.5\,\text{bar}}$$

$$\Delta G = -1971.85\,\text{J}$$

Molar Gibbs energy change = $\Delta G/n$ = –1971.85/2 = –985.9 J

5. Given: $n = 1\,\text{mol}, T = 300K, p_1 = 1\,\text{bar}, p_2 = 2\,\text{bar}, G_1 = 3.6\,\text{kJ}$

$$\Delta G = G_2 - G_1 = 2.303\, nRT \log\frac{p_2}{p_1}$$

$$G_2 = G_1 + 2.303\, nRT \log\frac{p_2}{p_1}$$

$$= -3600\,\text{J} + 2.303 \times 1\text{mol} \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 300\,\text{K} \times \log\frac{2\,\text{bar}}{1\text{bar}}$$

$$G_2 = -3600\,\text{J} + 1728.99\,\text{J} = -1871.01\text{J}$$

6. We know that the Gibbs expression corresponding to Helmholtz energy is

$$dA = -SdT - pdV$$

Differentiating with respect to $T$ at constant $V$ we get

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Differentiating the above equation with respect to $V$ at constant $T$ we get

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right)_T = -\left(\frac{\partial S}{\partial V}\right)_T$$

Differentiating the Gibbs equation with respect to $V$ at constant $T$ we get

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

Differentiating the above equation with respect to $T$ at constant $V$ we get

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right)_V = -\left(\frac{\partial p}{\partial T}\right)_V$$

Now, since $A$ is a state function, Euler's reciprocity relation is valid.
Therefore, we can write.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

This is the desired Maxwell relation.

7. We know that the standard Gibbs energy change for a reaction is given as

$$\Delta G^{\varphi} = \Delta H^{\varphi} - T\Delta S^{\varphi}$$

The change in standard enthalpy of formation is given as

$$\Delta H^{\varphi} = \sum \Delta H_f^{\varphi}(products) - \sum \Delta H_f^{\varphi}(reactants)$$

Substituting the values for the standard enthalpy changes for the products and the reactants, we get

$$\Delta H^{\phi} = (2 \times \Delta H_f^{\phi}(NH_3)) - \{\Delta H_f^{\phi}(N_2) + 3 \times \Delta H_f^{\phi}(H_2)\}$$

$$= \{(-46 \times 2) - (0 + (0 \times 3))\}\,\text{kJmol}^{-1} = -92\,\text{kJmol}^{-1}$$

The standard entropy change for the reaction is given as

$$\Delta S^{\varphi} = \sum S^{\varphi}(products) - \sum S^{\varphi}(reactants)$$

Substituting the values for the standard entropies for the products and the reactants, we get,

$$\Delta S^{\phi} = 2 \times S^{\phi}(NH_3) - \{S^{\phi}(N_2) + 3 \times S^{\phi}(H_2)\}$$

$$= \{(2 \times 193) - (192 + (3 \times 131))\}\,\text{JK}^{-1}\text{mol}^{-1}$$

$$= (386 - 585)\,\text{JK}^{-1}\text{mol}^{-1} = -199\,\text{JK}^{-1}\text{mol}^{-1}$$

Substituting the values of the change in standard enthalpy of formation and standard entropy change of the reaction in the expression for standard Gibbs energy change, we get

$$\Delta G^{\phi} = \{(-92.0k\text{Jmol}^{-1}) - (300\,\text{K} \times -199\,\text{JK}^{-1}\text{mol}^{-1})\}$$
$$= -32300\,\text{Jmol}^{-1} = -32.3\,\text{kJmol}^{-1}$$

*Since, the standard Gibbs energy change for the reaction is negative, the reaction will be spontaneous.*

## Terminal Questions

1. Spontaneity refers to the occurrence of a thermodynamic process on its own under a given set of conditions without the aid of any external agency.

   I. The reaction is always spontaneous if $\Delta U - T\Delta S < 0$. Therefore, the process will be spontaneous when $\Delta U < 0$ and $\Delta S > 0$.

   II. The reaction is always spontaneous if $\Delta H - T\Delta S < 0$. This will happen when $\Delta H < 0$ and $\Delta S > 0$

2. When $\Delta H > 0$ and $\Delta S < 0$; $\Delta G = \Delta H - T\Delta S$ will always be positive. Since the Gibbs energy change under the given set of conditions is always positive, the reaction will always be non-spontaneous.

3. The decrease in Helmholtz energy in an isothermal reversible process called work function as it is equal to all the types of work that the system can do.

   Gibbs energy is equal to work function, that is, $\Delta G = \Delta A$ for an ideal gas at constant temperature.

4. We know that:

   I. Helmholtz energy change for an isothermal reversible process is given as

   $$\Delta A = 2.303\, nRT \log \frac{p_2}{p_1}$$

   Given: $n = 2\,\text{mol}, T = 300\,\text{K}, p_1 = 5\,\text{bar}, p_2 = 1\,\text{bar}, R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

   Substituting the values, we get.

   $$\Delta A = 2.303 \times 2\,\text{mol} \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 300\,\text{K} \times \log \frac{5\,\text{bar}}{1\text{bar}} = 8030\,\text{J} = 8.03\,\text{kJ}$$

   Since, for an ideal gas at constant temperature, $\Delta G = \Delta A$, the change in Gibbs energy will be =8030 J =8.03 kJ

5. a. For a reversible process

   $$dA = -SdT - pdV$$

   i.e., $A = f(T,V)$

   $$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

   Comparing the coefficients of d$T$ we get $\left(\frac{\partial A}{\partial T}\right)_V = -S$

   b. Comparing the coefficients of d$p$we get $\left(\frac{\partial A}{\partial V}\right)_T = -p$

   c. For a reversible process

   $$dG = -SdT + Vdp$$

   $$G = f(T,p)$$

   $$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

   Comparing the coefficients of d$p$ we get $\left(\frac{\partial G}{\partial p}\right)_T = V$

   d. Comparing the coefficients of d$T$ we get $\left(\frac{\partial G}{\partial T}\right)_p = -S$

6. Standard Gibbs energy of a reaction is the difference between the total standard Gibbs energy of formation of the products and the total standard Gibbs energy of formation of the reactants. Mathematically,

   $$\Delta G^{\varphi} = \sum \Delta G_f^{\varphi}(products) - \sum \Delta G_f^{\varphi}(reac\tan ts)$$

7. $N_2O(g) + 3H_2(g) \rightarrow N_2H_2(g) + H_2O(g)$

   $$\Delta^{\phi} = H^{\phi} - T\Delta S^{\phi}$$

Given: $T = 300\,K$

$$\Delta H^{\varphi} \sum \Delta H_f^{\varphi}(products) - \sum \Delta H_f^{\varphi}(reac\tan ts)$$

$$\Delta H^{\varphi} = \Delta H_f^{\varphi}(N_2H_4) + \Delta H_f^{\varphi}(H_2O) - \{\Delta H_f^{\varphi}(N_2O) + 3 \times \Delta H_f^{\varphi}(H_2)\}$$

$$= \{(50 + -242) - (82 + 0 \times 3)\}\,\text{kJ} = -274\,\text{kJ}$$

$$\Delta S^{\phi} = \sum S^{\phi}(products) - \sum \Delta S^{\phi}(reac\tan ts)$$

$$\Delta S^{\phi} = S^{\phi}(N_2H_4) + S^{\phi}(H_2O) - \{S^{\phi}(N_2O) + 3 \times S^{\phi}(H_2)\}$$

$$= \{(120 + 189) - (220 + 3 \times 131)\}\,\text{JK}^{-1}$$

$$= (309 - 613)\,\text{JK}^{-1} = -304\,\text{JK}^{-1}$$

$$\Delta G^{\phi} = -274000\,\text{J} - (300\,\text{K} \times -304\,\text{JK}^{-1}) = -182800\,\text{J} = -182.8\,\text{kJ}$$

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# UNIT 2

# SYSTEMS OF VARIABLE COMPOSITION

## Structure

2.1 Introduction
  Expected Learning Outcomes
2.2 Partial Molar Quantities and Their Significance
  Relationship Between Thermodynamic Property and Partial Molar Properties
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## 2.1 INTRODUCTION

You have learnt earlier that the state of a thermodynamic system can be described in terms of four thermodynamic parameters. These are temperature, pressure, volume, and composition. You have also studied that various thermodynamic properties of the system change when the temperature, pressure and volume of the system are changed. Further, you also know that the extensive properties of the system depend on the amount (moles) of the substance present, for example, when the amount of the substance is doubled, the value of the extensive properties like internal energy, enthalpy, entropy, etc. of the system gets doubled. Have you wondered how the thermodynamic properties will be affected if the composition of the system is changed? In this unit, we will take up the issue of the effect of change in composition of the system on its thermodynamic properties. This aspect is particularly important in the application of thermodynamics to solutions and gaseous mixtures which in turn have a significant role to play in chemical process industries.

We will begin the unit by initiating a discussion on partial molar properties and attempt to understand their significance. This will be followed by a discussion on the experimental determination of partial molar volume-an important partial molar property of the system. Thereafter, we will dwell on an important quantity viz., chemical potential and outline its significance. We will also discuss the effect of pressure and temperature on this fundamental property. We will then take up systems consisting of mixtures of gases. In this context we will bring in the concept of fugacity and explain its significance. Towards the end of the unit, we would derive Gibbs-Duhem equation and discuss its importance.

In the next unit we will take up fundamentals of solid state.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- define partial molar quantities and outline their significance;
- differentiate between molar and partial molar properties;
- define and explain the term, partial molar volume;
- describe the method of experimental determination of partial molar volume;
- calculate partial molar volume of a component by using the mean molar volume versus mole fraction data;
- explain the term 'chemical potential' and state its significance;
- discuss the effect of temperature and pressure on chemical potential;
- explain the term 'fugacity' and state its significance; and
- derive Gibbs-Duhem equation and explain its importance.

## 2.2 PARTIAL MOLAR QUANTITIES AND THEIR SIGNIFICANCE

As stated above, we wish to understand the effect of change in the composition of the system on its thermodynamic properties. As you are aware the composition of a system comes into picture only when the system consists of more than one substance. Such a system having two or more substances is called a **mixture**. When the substances do not react with each other, we call them components of the system. In this unit we will discuss the systems having two components which do not react with each other. You would learn that the familiar thermodynamic properties of the system will need to be modified to include the effect of change in the composition of the system.

We are sure that you are familiar with the terms like solute, solvent, and solution. Here, we need to define a few more terms which will be useful in understanding the concepts being taken up later. A solution having one solvent and one solute has two components and is known as a **binary solution**. So, when we dissolve sodium chloride in water, we get a binary solution in which sodium chloride is the solute and water is the solvent. A solution having one solvent and two solutes that do not react has three components, therefore, it is known as a **ternary solution.** Similarly, a solute and two immiscible solvents also make a ternary solution.

The solute can be in the solid, liquid, or gaseous state. A solution formed by dissolving two solutes, say sodium chloride and potassium nitrate in water is an example of a ternary solution. In case both the components are liquid, the mixture is known as a solution only if both the liquids are completely miscible e.g., a mixture of alcohol and water. When the system consists of more than one gas, it is always known as a mixture of gases. A mixture of two gases is known as a binary mixture of gases.

To determine various properties of the mixture, we need to know how many components are present in the mixture and what is the amount of each one of them. You know that *the amount of each component in the mixture is expressed as the concentration of that component*. You would have learnt various ways to express the concentration of the components in a solution. In this unit, we will mainly use molarity, molality, and mole fractions. Let us quickly recall them.

***Molarity***, *c*, is defined as the moles of the solute per $dm^3$ (litre) of the solution. The concentration of component *i* is given as

$$c_i = \frac{n_i \times 1000}{V} \qquad \text{…(2.1)}$$

Here, $n_i$ is the amount of component *i* in moles and *V* is the volume of the solution. The unit of molarity is mol $dm^{-3}$. Since, volume is temperature dependent, molarity changes with the change in temperature.

***Molality***, *m* is defined at the amount of solute per kilogram of the solvent. The molarity of component *i* is given as

$$m_i = \frac{n_i \times 1000}{w} \qquad \text{…(2.2)}$$

Here, *w* is the mass of the solvent in gram. The unit of molality is mol $kg^{-1}$. It is important to note that contrary to molarity, the molality is not affected by the change in temperature.

***Mole fraction,*** $x_i$ of a component *i* is given as

$$\chi_i = \frac{n_i}{n_{total}} \qquad \text{… (2.3)}$$

Here, $n_{total}$ is the total amount of all the components in the mixture in moles. Mole fraction is unitless and it does not depend on the temperature of the system. For a two-component system having $n_A$ moles of component A and $n_B$ moles of component B, we can write,

$$\chi_A = \frac{n_A}{n_A + n_B} \text{ and } \chi_B = \frac{n_B}{n_A + n_B} \qquad \text{…(2.4)}$$

Also,

$$\chi_A + \chi_B = 1 \quad \text{...(2.5)}$$

Solve the following simple questions to assess your understanding of concentration terms defined above.

---

## *SAQ 1*

Calculate the following:

a) the molarity of a solution whose 100 $cm^3$ contain0.630 g of oxalic acid

b) the molality of a solution prepared by dissolving0.630 g of pure oxalic acidin100 g of water

c) You may use the molar mass of oxalic acid as 126 g $mol^{-1}$.

---

## *SAQ 2*

Calculate the mole fraction of ethanol in the following solutions.

a) a solution prepared by mixing 23 g of ethanol and 180 g of water, and

b) a solution prepared by mixing 18 g of waterin 100g of ethanol.

c) You can use the molar mass of ethanol and water as 46 g $mol^{-1}$ and 18.0 g $mol^{-1}$, respectively.

---

## 2.2.1 Partial Molar Properties

You know that the extensive properties depend on the amount (in moles) of the substance. If we divide such a property by the number of moles, we will get the corresponding molar properties i.e., property per mole of the substance. For example, if we represent a thermodynamic property (*V*, *U*, *H*, *A* or *G*) by *X*, then the molar value of the property *X* will be given as

$$X_m = \frac{X}{n} = \frac{\text{Value of thermodynamic property of the system}}{\text{amount of the system (in moles)}} \quad \text{...(2.6)}$$

You may note that the molar properties are represented by suffixing *m* to the symbol of the property. Thus, the volume of one mole of a substance, is known as the **molar volume** and is represented as:

$$V_m = \frac{V}{n} \quad \text{...(2.7)}$$

Here, V is the volume of the system having n moles of the substance. Now, you may ask that molar properties are fine but what is a partial molar property and why do we need it? Also, when do we use molar property and when do we use partial molar property? Let us answer the second question first. We use molar property when the system consists of a pure substance and partial molar property when the system has two or more components. This will get clearer as we move ahead. Let us now try to understand what are partial molar properties and why do we need them in the systems having two or more components?

Let us write the mathematical expression for the change in thermodynamic property, *X*, with the change in the composition of the system. First, we will do so for the change in the thermodynamic property for a pure substance or a one component system. You know that for a one component system, the extensive properties like internal energy, enthalpy, entropy, and Gibbs energy depend upon the temperature, pressure, and amount. This fact is represented mathematically as

$$X = f\left(T, p, n\right) \qquad \ldots(2.8)$$

That is, the property is a function of *T*, *p*, and *n*. Here, *X* is said to be a dependent variable which depends on the values of *T, p* and *n,* which can be varied independent of each other and are called independent variables. We can take a case where, we keep two (say *p* and *n*) variables constant and vary one of the variables (say *T*). This will bring in certain change in the property. Similarly, we can change *p* or *n* while keeping (*T*&*n)*and (*T* &*p*)respectively as constant. The total change in the thermodynamic property can then be expressed as

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial X}{\partial p}\right)_{T,n} \mathrm{d}p + \left(\frac{\partial X}{\partial n}\right)_{T,p} \mathrm{d}n \qquad \ldots.\ (2.9)$$

Where, the differential in the first term on the right, $\left(\frac{\partial X}{\partial T}\right)_{p,n}$ represents the change in the property *X* when the temperature of the system is changed, while keeping the pressure *p* and amount *n* constant. In other words, this term represents the rate of change of the property, *X* as a function of temperature when*p* and *n* are kept constant. Whereas $\mathrm{d}T$ represents the total change in the temperature. The differential in the second term in Eq. (2.9) viz., $\left(\frac{\partial X}{\partial p}\right)_{T,n}$ represents the change in the property *X* when the pressure is changed, while the temperature *T* and amount *n* are kept constant and $\mathrm{d}p$ is the total change in pressure. Similarly, the third term, $\left(\frac{\partial X}{\partial n}\right)_{T,p}$ represents the change in property *X* when the amount, $n$ is changed while the temperature and pressure are kept constant and $\mathrm{d}n$ is the total change in the amount.

The terms $\left(\frac{\partial X}{\partial T}\right)_{p,n}$, $\left(\frac{\partial X}{\partial p}\right)_{T,n}$ and $\left(\frac{\partial X}{\partial n}\right)_{T,p}$ are known as the partial derivatives and indicate how the property *X* changes when one of the variables is changed while keeping the other two variables constant.

Let us now extend the argument to a binary mixture which has $n_A$ moles of component A and $n_B$ moles of component B and work out corresponding expression for the change in the property *X*. The thermodynamic property in this case will depend upon temperature, pressure, $n_A$ and $n_B$. Therefore, the expression for the dependent variable, *X* becomes

$$X = f(T, p, n_A, n_B) \qquad \ldots.\ (2.10)$$

Where, *T, p,* $n_A$ and $n_B$ are the independent variables. Using similar method as above, we can write the expression for the total change in *X* as follows

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{p,n_A,n_B} \mathrm{d}T + \left(\frac{\partial X}{\partial p}\right)_{p,n_A,n_B} \mathrm{d}p + \left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B} \mathrm{d}n_A + \left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A} \mathrm{d}n_B \qquad \ldots(2.11)$$

You can note that the thermodynamic property $X$ changes with the changes in $T$, $p$, $n_A$ and $n_B$. Now, if we wish to know the change in the property on changing $n_A$ and $n_B$ while keeping the temperature and pressure as constant. In such a case since $\mathrm{d}T = 0$ and $\mathrm{d}p = 0$; the Eq. (2.11) would get modified as

$$\mathrm{d}X = \left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B} \mathrm{d}n_A + \left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A} \mathrm{d}n_B \qquad \ldots(2.12)$$

The terms $\left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B}$ and $\left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A}$ are the partial derivatives of the property with respect to the number of moles of the components i.e., $n_A$ and $n_B$, respectively. These terms are known as ***partial molar properties***. Here, $\left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B}$ represents the partial molar property for the component A while $\left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A}$ represents the partial molar property for the component B.

To understand the physical significance of the term partial molar property, let us consider a situation wherein we take a large volume of the binary mixture and add one mole of component A to it i.e., $(\mathrm{d}n_A = 1)$.Since we have taken a large volume, the mole fraction of component B practically does not change i.e., $(\mathrm{d}n_B = 0)$. Substituting in Eq. (2.12) we get,

$$\mathrm{d}X = \left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B} \qquad \ldots(2.13)$$

Thus, the partial molar property of component A in a mixture can be defined as the change in the property $X$ of the mixture when one mole of component A is added to a large volume of mixture at constant temperature& pressure and keeping the amounts (number of moles) of remaining components constant. The partial molar properties are represented either as $X_{i,m}$ or $\bar{X}_i$ where the subscript $i$ represents the component whose amount is being varied and the subscript $m$(as stated before)or a bar on top of the symbol of the property indicates the property to be molar.Using such are presentation for partial molar properties, Eq.(2.12) can be written as

$$\mathrm{d}X = X_{A,m}\mathrm{d}n_A + X_{B,m}\mathrm{d}n_B \qquad \ldots(2.14)$$

Here, $\mathrm{d}X$ is the total change in property $X$ due to change in composition at constant temperature and pressure. Similarly, other extensive thermodynamic properties can also be written in terms of partial molar properties for systems having more than one component. Various partial molar properties of a binary mixture are summarised in Table 2.1.

The partial molar quantities are intensive properties and depend upon the temperature, pressure, and the composition.

It is important to note here that the partial molar quantities are intensive properties. These depend upon the temperature, pressure, and composition. In other words, the partial molar quantity will not change if the amount of a component is changed in such a way that the concentration / composition of the mixture does not change.

For example, in a binary solution, if the number of moles of A as well asthatof B is doubled then the composition of the solution will not change. Therefore, the partial molar properties will also not change. However, if the moles of A are doubled and that of B are not changed, then the composition of the solution changes. In this case the partial molar properties of the solution will also change.

**Table2.1:Expressions and symbolsfor different Partial Molar Properties for a binary mixture**

| **Thermodynamic Property** | **Partial Molar Property** | | |
|---|---|---|---|
| | **Name** | **Symbol** | **Expression** |
| Volume<br>$V = f(T, p, n_A, n_B)$ | Partial molar volume | $V_{i,m}$ or $\bar{V}_i$ | $\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j}$ |
| Internal energy<br>$U = f(T, p, n_A, n_B)$ | Partial molar internal energy | $U_{i,m}$ or $\bar{U}_i$ | $\left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_j}$ |
| Enthalpy<br>$H = f(T, p, n_A, n_B)$ | Partial molar enthalpy | $H_{i,m}$ or $\bar{H}_i$ | $\left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_j}$ |
| Entropy<br>$S = f(T, p, n_A, n_B)$ | Partial molar entropy | $S_{i,m}$ or $\bar{S}_i$ | $\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j}$ |
| Gibbs energy<br>$G = f(T, p, n_A, n_B)$ | Partial molar Gibbs energy(Chemical potential) | $G_{i,m}$ or $\bar{G}_i$ | $\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$ |

If we extend the argument to a multicomponent mixture, the thermodynamic property will depend upon temperature, pressure, $n_A$, $n_B$ the mole fraction of other components. That is,

$$X = f(T, p, n_A, n_B, ......) \quad .... (2.15)$$

For an infinitesimal change in the temperature, pressure, and the amounts of all the components, the change in the property X will be given as

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{p,n_A,n_B,n...} \mathrm{d}T + \left(\frac{\partial X}{\partial p}\right)_{p,n_A,n_B,n...} \mathrm{d}p + \left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B,n...} \mathrm{d}n_A$$
$$+ \left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A,n...} \mathrm{d}n_B + \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_A,n_B,n_j......} \mathrm{d}n_i + ..... \quad .... (2.16)$$

Under constant temperature and constant pressure conditions, the expression becomes

$$\mathrm{d}X = \left(\frac{\partial X}{\partial n_A}\right)_{T,p,n_B,n...} \mathrm{d}n_A + \left(\frac{\partial X}{\partial n_B}\right)_{T,p,n_A,n...} \mathrm{d}n_B + \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_A,n_B,n_j......} \mathrm{d}n_i + .... \quad .... (2.17)$$

Using the representation of partial molar quantities, the expression becomes

$$\mathrm{d}X = X_{A,m}\mathrm{d}n_A + X_{B,m}\mathrm{d}n_B + X_{i,m}\mathrm{d}n_i + ..... \quad ...(2.18)$$

Having learnt about the partial molar quantities and their representation let us learn about the use of partial molar properties. Partial molar properties are quite important in thermodynamic studies of the systems having variable compositions. The values of partial molar properties help usin deducing the type of interactions between various components in a mixture. If the composition of the mixture and the partial molar quantities of all the components of the mixture at that composition are known The value of any thermodynamic property can be calculated at a given temperature, pressure, and composition of the mixture. Let us derive a general mathematical expression for calculating the thermodynamic property from the partial molar properties in a binary mixture.

## 2.2.2 Relationship between Thermodynamic Property and Partial Molar Properties

As you already know, the mole fraction for component A in a mixture containing $n_A$ moles of A and $n_B$ moles of B can be written as

$$\chi_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n} \Rightarrow n_A = \chi_A . n \qquad \ldots(2.19)$$

Here, $n$ is equal to the sum of the number of moles of A and B. Similarly, for component B, we can write

$$n_B = \chi_B . n \qquad \ldots(2.20)$$

To keep the composition of the mixture constant, $n_A$ and $n_B$ should be changed in such a way that $\chi_A$ and $\chi_B$ do not change. Let us increase the total amount of A and B (i.e., $n_A + n_B$) from $n$ moles to $kn$ moles. If we represent the change in moles of A as $dn_A$; the change in moles of B as $dn_B$ and the change in total moles as $dn$, then we can write

$$\mathrm{d}n_A = \chi_A \mathrm{d}n \qquad \ldots(2.21)$$

$$\mathrm{d}n_B = \chi_B \mathrm{d}n \qquad \ldots(2.22)$$

$$\mathrm{d}n = kn - n = n(k-1) \qquad \ldots(2.23)$$

Here $\chi_A$ and $\chi_B$ are not changing as we change the amount of A and B.

Substituting the values of $\mathrm{d}n_A$ and $\mathrm{d}n_B$ in Eq. (2.14) we get,

$$\mathrm{d}X = X_{A,m}\chi_A \mathrm{d}n + X_{B,m}\chi_B \mathrm{d}n \qquad \ldots(2.24)$$

Now, to find the total value of *X*, Eq. (2.24) needs to be integrated from the initial amount (*n*) of the mixture to the final amount (*kn*). Since, *X* is an extensive property, if *n* is changed by *k* times, *X* will also change by *k* times. Therefore, the integration of Eq. (2.24) will have the following expression

$$\int_X^{kX} \mathrm{d}X = \int_n^{kn} (X_{A,m}\chi_A + X_{B,m}\chi_B)\mathrm{d}n \qquad \ldots(2.25)$$

You would recall that we have changed the composition in such a way that the mole fractions of the two components do not change. Since, the partial molar quantities are also constant, the term in the bracket on the right side of the equation will be constant.

So, we can write

$$(kX - X) = (X_{A,m}\chi_A + X_{B,m}\chi_B)\int_{n}^{kn} dn \qquad \ldots(2.26)$$

Simplifying, we get

$$X(k-1) = (X_{A,m}\chi_A + X_{B,m}\chi_B)(k-1)n \qquad \ldots(2.27)$$

Substituting for $\chi_A$ & $\chi_B$ and simplifying, we get

$$X = X_{A,m}n_A + X_{B,m}n_B \qquad \ldots(2.28)$$

This is the desired relationship between thermodynamic property, and the partial molar properties of the components in a binary mixture. For a mixture having more than two components this expression can be generalised as follows

$$X = \sum_i X_{i,m}n_i \qquad \ldots(2.29)$$

To have a clearer understanding of partial molar properties we take the case of partial molar volume. The volume is a good choice as it is an extensive property that can be easily visualised. However, before that answer the following simple question to assess your understanding.

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*SAQ 3*

Partial molar temperature for a mixture is irrelevant. Explain.

---

## 2.3 PARTIAL MOLAR VOLUME

We know that if we add 100 cm$^3$ of water to one litre (1000 cm$^3$) of water, the total volume of water increases and becomes 1100 cm$^3$. However, it is observed that if 100 cm$^3$ of water is added to one dm$^3$of a binary aqueous solution (say of ethanol and water) at a constant temperature and pressure, the total volume of the solution generally increases, but it may or may not become 1100 cm$^3$.That is, the increase in volume of the mixture may not be equal to 100 cm$^3$.The molar volume of water i.e., the volume of 1 mole of pure water at 298 K and 1bar is 18.07 cm$^3$ mol$^{-1}$. So, when one mole of water is added to a large volume of pure substance B, we expect the volume of the resulting solution to increase by the molar volume of water (i.e.,18.07 cm$^3$). In some cases, the increase in the volume of the solution is equal to the molar volume of the added component. However, it has been observed that generally the increase in the volume of the solution is different from the molar volume of the added component.

There are two questions now,

I. Why the total volume of the solution is not equal to the sum of the volume of the solution and the volume of the added component?

II. Can we calculate or predict the change in the total volume of a solution when a given volume of one component is added to it at constant temperature, pressure while keeping the amount of the rest of the components constant?

Let us try to find answers to these

In a pure substance (one component system), a given molecule is surrounded by same type of molecules, and therefore, the intermolecular forces between them are same. These intermolecular forces do not change on further addition of one mole of the pure substance to it as there are no new interactions. As a consequence, the change in volume is equal to the molar volume of the added component. On the other hand, in a mixture (say a binary mixture of A and B) a given molecule is surrounded by different types of molecules. Consequently, different types of intermolecular forces exist between the molecules in the mixture. This affects the arrangement of molecules with respect to each other.

In such a case, when we add a mole of one of the components then the increase in volume will depend on the nature of interaction between the molecules. If the nature of intermolecular forces in the pure solvent and in the solution are similar, then the increase in the volume of the mixture will be similar to the molar volume of the added component. On the other hand, if these forces are of different nature, then the increase in the volume of the mixture will be different from molar volume of the added component in the pure form.

The answer to the second question is 'yes'. For this, let us derive a general expression for the change in the volume of the mixture in terms of partial molar volumes of its components. For this, we will proceed in the same way as we did while deriving the general expression for partial molar properties. Volume of a binary solution which depends on temperature, pressure, amount of A and the amount of B can be expressed as

$$V = f(T, p, n_A, n_B) \qquad \ldots(2.30)$$

Using Eq. (2.12) we can write the expression for change in the total volume of the binary mixture with the change in the amounts of components A and B at constant temperature and pressure as follows.

$$\mathrm{d}V = \left(\frac{\partial V}{\partial n_A}\right)_{T,p,n_B} \mathrm{d}n_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,p,n_A} \mathrm{d}n_B \qquad \ldots(2.31)$$

Here, $\left(\frac{\partial V}{\partial n_A}\right)_{T,p,n_B}$ is the *partial molar volume* of A and $\left(\frac{\partial V}{\partial n_B}\right)_{T,p,n_A}$ is equal to *partial molar volume* of B.

Now, suppose we add 1 mole of the component A to the mixture at constant temperature, pressure, and the number of moles of B. In such a case, $\mathrm{d}n_A = 1$ and $\mathrm{d}n_B = 0$. Substituting in Eq. (2.31), we get.

$$\mathrm{d}V = \left(\frac{\partial V}{\partial n_A}\right)_{T,p,n_B} \qquad \ldots(2.32)$$

This expression provides us the definition of partial molar volume. Thus, *the partial molar volume of component A in a binary mixture may be defined as the change in the volume of a mixture when one mole of component A is added to a large volume of mixture at constant temperature, pressure while keeping the number of moles of component B constant.* The unit of partial molar volume is $\mathrm{dm}^3\ \mathrm{mol}^{-1}$.

Using the notation of partial molar properties as given above, we can write the expression for the change in volume of the binary mixture in terms of partial molar volumes of the components A and B as follows:

$$\mathrm{d}V = V_{A,m}\mathrm{d}n_A + V_{B,m}\mathrm{d}n_B \qquad \text{… (2.33)}$$

The total volume of a binary mixture when $n_A$ moles of component A are mixed with $n_B$ moles of component B at constant temperature and pressure is given by the following expression

$$V = V_{m,A}n_A + V_{m,B}n_B \qquad \text{…(2.34)}$$

**Partial molar volume: a physical insight**

Let us try to have an insight into the concept of molar volume by taking the example of binary solution containing water (substance A) and methanol (substance B). The partial molar volume of the methanol here will be the rate at which the volume of the binary solution changes with the amount of methanol added to a large volume of the mixture at constant temperature and pressure i.e.,

$$V_{m,\mathrm{B}} = \left(\frac{\partial V}{\partial n_B}\right)_{T,p,n_A} \qquad \text{…(2.35)}$$

At 25°C and 1 bar, the molar volume of pure water is $V^*_{\mathrm{m,A}} = 18.07\,\mathrm{cm^3\ mol^{-1}}$ and that of pure methanol is $V^*_{\mathrm{m,B}} = 40.75\,\mathrm{cm^3\ mol^{-1}}$. When we mix 100.0 $\mathrm{cm^3}$ of water at 25°C with 100.0$\mathrm{cm^3}$ of methanol at same temperature, it is found that the volume of the resulting mixture is193.1 $\mathrm{cm^3}$and not equal to the sum of the volumes added i.e., 200.0 $\mathrm{cm^3}$. Let us calculate the composition of this mixture:

$$n_\mathrm{A} = \frac{V^*_\mathrm{A}}{V^*_\mathrm{m,A}} = \frac{100.0\,\mathrm{cm^3}}{18.07\,\mathrm{cm^3\ mol^{-1}}} = 5.53\,\mathrm{mol} \qquad \text{…(2.36)}$$

$$n_\mathrm{B} = \frac{V^*_\mathrm{B}}{V^*_\mathrm{m,B}} = \frac{100.0\,\mathrm{cm^3}}{40.75\,\mathrm{cm^3\ mol^{-1}}} = 2.45\,\mathrm{mol} \qquad \text{…(2.37)}$$

$$x_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A} + n_\mathrm{B}} = \frac{2.45\,\mathrm{mol}}{5.53\,\mathrm{mol} + 2.45\,\mathrm{mol}} = 0.307 \qquad \text{…(2.38)}$$

Now, if we prepare a mixture by mixing5.0$\mathrm{dm^3}$of water (277.78 moles) and5.0$\mathrm{dm^3}$ of methanol (122.5 moles) i.e., 50 times the volumes used in above case, the volume of the mixture will also be 50 times i.e., 9.655$\mathrm{dm^3}$. However, it will have the same mole fraction of methanol i.e., 0.307.

On adding 40.75 $\mathrm{cm^3}$ (one mole) of pure methanol to the above solution it is found that the volume increases by only 38.8 $\mathrm{cm^3}$.Similarly, on addingone mole(40.75 $\mathrm{cm^3}$) of pure methanol to the solution prepared by mixing 10.0 $\mathrm{dm^3}$ of water and 10.0 $\mathrm{dm^3}$ of methanol, again the volume increases by only 38.8 $\mathrm{cm^3}$.Let us calculate the mole fractions of these solutions and compare as given in Table 2.2.

**Table 2.2: Data pertaining to the example being discussed.**

| S. No. | Volume (in cm$^3$) (No. of moles) of water | Volume (in cm$^3$) (No. of moles) of methanol | Total observed volume (in cm$^3$) | Mole fraction of water ($X_A$) | Mole fraction of methanol ($X_B$) |
|---|---|---|---|---|---|
| 1 | 100.0 (5.53) | 100.0(2.45) | 193.1 | 0.693 | 0.307 |
| | | | | | |
| 2 | 5000 (277.78) | 5000 (122.5) | 9655 | 0.693 | 0.307 |
| | **Adding 40.75 cm$^3$ (one mole) of pure methanol** | | | | |
| | 5000 (277.78) | 50407.5 (123.5) | 9.6938 | 0.6922 | 0.3078 |
| | | | | | |
| 3 | 10000 (555.56) | 10000 (245.0) | 193100 | 0.693 | 0.307 |
| | **Adding 40.75 cm$^3$ (one mole) of pure methanol** | | | | |
| | 10000 (555.56) | 10040.75 (246.0) | 19338.8 | 0.693 | 0.307 |

The amount of methanol added (40.75 cm$^3$, 1 mole) in the examples above is not infinitesimal, but it is quite small as compared to the amounts in the initial mixture. Therefore, as shown in Table 2.1 there is very little change in the composition of the mixture. We can say that in these additions the mole fraction of water ( $n_A$ ) remains constant. The observed change in the volume (38.8 cm$^3$) of the mixture on adding 1 mole of methanol is the partial molar volume of methanol as it corresponds to the change in volume per mole of methanol at constant $T$, $p$ and $n_A$ .In other words,

$$V_{m,\mathrm{B}} = \left(\frac{\Delta V}{\Delta n_B}\right)_{T,p,n_A} = \frac{\Delta V}{\Delta n_B} = 38.8\,\mathrm{cm^3\,mol^{-1}}.$$

Thus, as defined above, the partial molar volume of component B is the volume change per mole of the component B added to such a large volume of the mixture such that its composition is not appreciably affected. Nowif instead of methanol, we had chosen to add a mole of water (18.07 cm$^3$) to different volumes of the mixture then the change in the volume of the mixture would have been 17.74 cm$^3$. This is the partial molar volume of water at this composition. Thus, the partial molar volumes of methanol and water in a solution having mole fraction of methanol=0.307 are 38.8 cm$^3$ mol$^{-1}$and 17.74 cm$^3$mol$^{-1}$respectively.

**Imp:** The data and the calculations in this example are for a mixture of water and methanol having the mole fractions as 0.693 and 0.307 respectively. Had we used any other composition, the corresponding partial molar volumes would have been different.

Let us take some examples to learn about the applications of the expressions derived for partial molar volumes.

**Example 2.1**: The partial molar volumes of water and methanol in a solution having 5.53 mol of water and 2.45 mol of methanol at 298 K and 1 bar pressure are 17.74 cm$^3$ mol$^{-1}$ and 38.8 cm$^3$ mol$^{-1}$ respectively. Calculate the total volume of the solution

**Solution**: Using Eq. (2.34) we can write, total volume,

$$V = V_{m,W}n_W + V_{m,M}n_M$$

Given: $n_W$ = 5.53 mol & $n_M$ = 2.45 mol

$V_{m,W}$ = 17.74 cm$^3$ mol$^{-1}$& $V_{m,M}$ = 38.8 cm$^3$ mol$^{-1}$

Substituting the values in the expression for total volume, we get

$$V_t = (17.74\,\text{cm}^3\,\text{mol}^{-1} \times 5.53\,\text{mol}) + (38.8\,\text{cm}^3\,\text{mol}^{-1} \times 2.45\,\text{mol}) = 193.16\,\text{cm}^3$$

Thus, the volume of the solution would be = 193.16 cm$^3$

**Example 2.2:** Calculate the volumes of pure methanol and pure water at 25°C that must be mixed to form 1000 cm$^3$ solution of methanol in water having a mole fraction of 0.3. The molar volumes of pure methanol and water and their partial molar volumes for this composition and temperature are given as under

$$V_{m,M} = 38.63\,\text{cm}^3\text{mol}^{-1} \quad \& \quad V^*_{m,M} = 40.73\,\text{cm}^3\text{mol}^{-1}$$

$$V_{m,W} = 17.77\,\text{cm}^3\text{mol}^{-1} \quad \& \quad V^*_{m,W} = 18.07\,\text{cm}^3\text{mol}^{-1}$$

**Solution:** According to Eq. (2.34) we can write the expression for the molar volume of the mixture as

$$V = V_{m,W}n_W + V_{m,M}n_M$$

Substituting the values of mole fractions and the partial molar volumes, we get the molar volume of the mixture as

$$V = (17.77 \times 0.7) + (38.63 \times 0.3) = 24.03\ \text{cm}^3\text{mol}^{-1}$$

Now, since we need 1000 cm$^3$ of the mixture, the total number of moles of the solution required will be:

$$n = \frac{1000\ \text{cm}^3}{24.03\ \text{cm}^3\text{mol}^{-1}} = 41.61\,\text{mol}$$

We are given that the mole percentage of methanol is 30%. It implies that the number of moles of methanol in the mixture will be

$$n_M = (0.3)(41.61) = 12.48\,\text{mol}$$

and that of water will be $n_W = (0.7)(41.61) = 29.13$

The volume of each pure species required will be given as: $V_i = n_i V^*_{m,i}$ cm$^3$

thus, $V_M = 12.48 \times 40.73\ \text{cm}^3 = 508.31\text{cm}^3$ and

$$V_W = 29.13 \times 18.07\ \text{cm}^3 = 526.38\,\text{cm}^3$$

It is interesting to note here that the total volume of the pure components added is $(508.31\text{cm}^3 + 526.38\text{cm}^3 = 1034.69\ \text{cm}^3)$ is more than the total volume of the solution. This is due to the fact that the partial molar volumes at this composition are smaller than the molar volumes of the pure species.

### 2.3.1 Volume of Mixing

From the discussion on partial molar volumes, you now understand that when we mix 50 $cm^3$ of component A and 50 $cm^3$ of component B, the volume of the binary solution formed may or may not be equal to 100 $cm^3$. Let us now try to learn how much could be the change in the volume of solution from the total volume of combining components. This difference is called volume of mixing($\Delta_{mix}V$) and is equal to the difference between the volume of the solution and the sum of the volumes of the pure components. That is, we can write the expression for volume of mixing as:

$$\Delta_{mix}V = V_{A,m}n_A + V_{B,m}n_B - (V^*_{A,m}n_A + V^*_{B,m}n_B) \qquad \text{…(2.39)}$$

Here the sum of first two terms gives the volume of the solution. $V^*_{A,m}$ and $V^*_{B,m}$ are the molar volumes of pure A and pure B components respectivelyand the term in the brackets $(V^*_{A,m}n_A + V^*_{B,m}n_B)$ is the sum of the volumes of pure A and pure B components.

The volume of mixing of two components can be zero or non-zero depending on the nature and magnitude of intermolecular interactions between similar and dissimilar molecules. When the interactions between the molecules of two components (A-B) are equal to the A-A and B-B interactions then the volume of mixture is equal to the total volume of the pure components. This means that the volume of mixing ($\Delta_{mix}V$) is zero. Such a solution or a mixture is known as an **ideal solution** or an **ideal mixture**. The total volume of an ideal solution can therefore be written as

$$V = V^*_{A,m}n_A + V^*_{B,m}n_B \qquad \text{…(2.40)}$$

Dividing Eq. (12.40)throughout by the total amount (moles) of the solution, *n* we get the expression for **mean molar volume** of the solution ($V_m$). That is,

$$V_m = \frac{V}{n} = V^*_{A,m}\frac{n_A}{n} + V^*_{B,m}\frac{n_B}{n} \qquad \text{…(2.41)}$$

Or we can write,

$$V_m = V^*_{A,m}\chi_A + V^*_{B,m}\chi_B \qquad \text{…(2.42)}$$

If we plot a graph between mean molar volume of the solution versus mole fraction of component B, ($\chi_B$), we will get a straight line with the intercept as $V^*_{A,m}$ at $\chi_B = 0$. On the other hand, the intercept at $\chi_B = 1$ will be equal to $V^*_{B,m}$. Thus, for an ideal two-component solution, the volume of the solution varies linearly with the concentration of the solution as shown inFig.2.1.

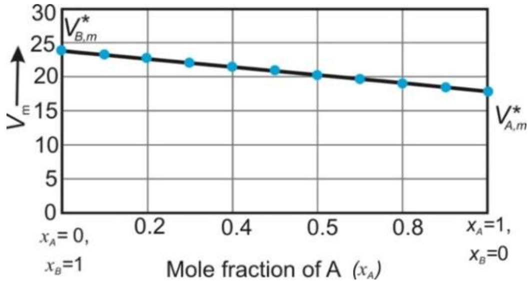
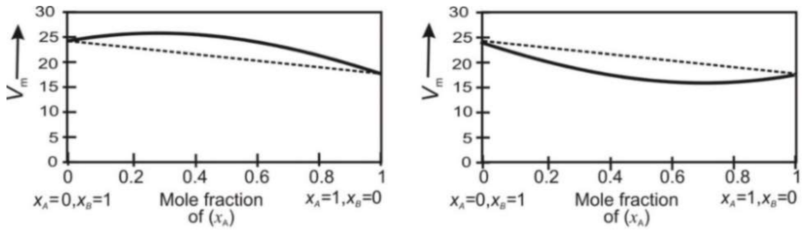


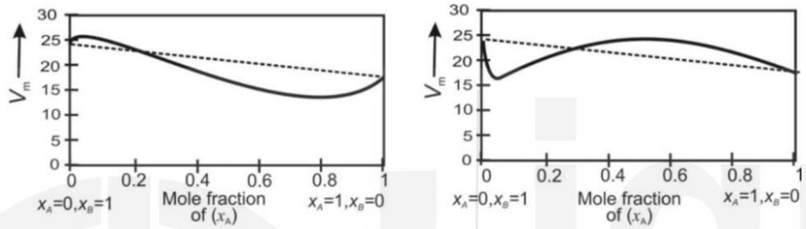
**Fig.2.1:Variation of the volume of an ideal two-component solution with the concentration of the solution.**

When the interactions between the unlike molecules of the two components (A and B) are not equal to the interactions between like molecules(A-A and B-B)of the pure components, then the volume of the solution is not equal to the sum of the volumes of the pure components. Hence, the $\Delta_{mix}V$ is not equal to zero. Such a solution is known as a **non-ideal solution**. That is,

$$V_{A,m}n_A + V_{B,m}n_B \neq (V^*_{A,m}n_A + V^*_{B,m}n_B) \qquad \ldots(2.43)$$



$\Delta_{mix}V>0$ $\Delta_{mix}V<0$



initially$\Delta_{mix}V>0$ and then $\Delta_{mix}V<0$ initially$\Delta_{mix}V<0$ and then $\Delta_{mix}V>0$

**Fig. 2.2: Different types of plots of the variation of molar volume of the solution as a function of mole fraction. The dotted lines represent $\Delta_{mix}V = 0$**

In case of non-ideal solutions, the volume of the solution varies non-linearly with concentration. The nature of variation of volume of the solution will depend upon the nature and magnitude of A-A, B-B and A-B intermolecular interactions between the two components. These interactions will manifest in terms of the difference in volume of mixing. Accordingly, the nature of the variation of volume of the non-ideal solution with concentration will be of any one of the four possible types. These types along with their representative plots for variation are given in Fig. (2.2)

Let us now take up the experimental determination of partial molar volumes. However, before that answer the following simple question to assess your understanding.

## *SAQ 4*

2.0 moles of pure ethanol is added to 2.0 moles of pure water. If the partial molar volume of ethanol and water for $\chi_A = \chi_B = 0.5$ are 57.4 cm$^3$mol$^{-1}$ and 16.9 cm$^3$mol$^{-1}$respectively, calculate the total volume of the solution.

## 2.3.2 Experimental Determination of Partial Molar Volume

Determination of partial molar volume helps in understanding the nature of interactions between the components of the solution. Such determinations of partial molar volume are also of interest because of their thermodynamic relationship with other partial molar quantities like partial molar Gibbs energy i.e., *chemical potential*.

As explained above, the mean molar volume for a non-ideal binary solution is given as

$$V_m = V_{A,m}\chi_A + V_{B,m}\chi_B \qquad \ldots(2.44)$$

Since $\chi_A + \chi_B = 1$, we can substitute $(\chi_B)$ by $(1-\chi_A)$ to get

$$V_m = V_{A,m}\chi_A + V_{B,m}(1-\chi_A) \qquad \ldots(2.45)$$

Rearranging, the equation, we get

$$V_m = (V_{A,m} - V_{B,m})\chi_A + V_{B,m} \qquad \ldots(2.46)$$

Thus, according to Eq. (2.46) a plot of mean molar volume as a function of the mole fraction of component A will give a straight line with slope and intercept as $(V_{A,m} - V_{B,m})$ and $(V_{B,m})$ respectively.

In a typical experimental determination of partial molar volume, a series of binary solutions of A and B are prepared with varying mole fractions of A. Then the volume of each solution is measured, and the mean molar volume is calculated for each composition. A graph of $V_m$ is then plotted against the mole fraction of component A ( $\chi_A$ ). This graph may or may not be a straight line depending upon the nature of the two components as discussed above. A linear plot suggests that the partial molar volumes are independent of the composition and are expected to be equal to the molar volumes of respective pure components.

In case of non-linear variation of mean molar volume with mole fraction of component A, the molar volumes of the components ( $V_{A,m}$ and $V_{B,m}$ ) are dependent upon the composition of the solution. That is, at each value of $\chi_A$ the partial molar volumes are different. However, for a given composition, $V_{A,m}$ and $V_{B,m}$ are constant. Therefore, the slope of the tangent drawn at any given point on the curve along with the corresponding intercept can be used to calculate the partial molar volumes of the two components for the composition corresponding to the point. The slope of the tangent can be obtained by differentiating Eq. (2.46) with respect to $\chi_A$

$$\text{The slope of the tangent} = \left(\frac{\partial V_m}{\partial x_A}\right) = (V_{A,m} - V_{B,m}) \qquad \ldots(2.47)$$

Further, as per Eq. (2.46) the intercept for the tangent at $\chi'_A$ is equal to $V_{B,m}$.

Therefore, to determine the partial molar volumes at a given composition, $\chi'_A$ a tangent to the curve is drawn at $\chi'_A$ and the slope and the intercept are measured. These can then be used to determine the partial molar volumes.

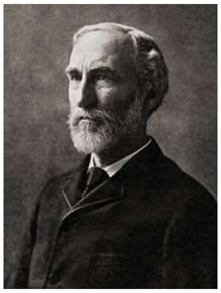
Partial molar volume for component B for composition, $\chi'_A$ = $V_{B,m}$ = intercept

Partial molar volume for component A for composition, $\chi'_A$ = $V_{A,m}$

= slope + intercept = $(V_{A,m} - V_{B,m})$ + $V_{B,m}$

Having learnt about partial molar volume and its determination, let us now take up a very important partial molar property, viz., Chemical potential.

## 2.4 CHEMICAL POTENTIAL



Josiah Williards Gibbs (1839 –1903). **Source: Wikipedia**

In this section you are going to learn about probably the most important partial molar property with a special name-**chemical potential**. You have studied in earlier classes and in the previous unitthat Gibbs energy plays an important role in predicting the feasibility of a process. In a system having many components, instead of Gibbs energy of pure components, partial molar Gibbs energy values of all the components are used to predict the feasibility and the direction of the process. The partial molar Gibbs energies are also importantin the study of chemical equilibrium and phase equilibrium. Due to the importance of partial molar Gibbs energy in thermodynamic studies, it was given a special name c*hemical potential* by American scientist Josiah Williards Gibbs (1839 –1903). The chemical potential is represented by the symbol $\mu$ and is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad \text{…(2.48)}$$

That is, the chemical potential of the $i$ th component ( $\mu_i$ ) refers to the rate of change of Gibbs energy with the change in the number of moles of $i$ the component when temperature, pressure and the number of moles of all other components are kept constant.

As discussed above, Gibbs energy, *G* depends upon temperature, pressure, and composition i.e.,

$$G = \mathrm{f}(T, p, n_A, n_B) \qquad \text{….(2.49)}$$

Using Eq. (2.11) we can write the expression for total change in Gibbs energy as

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_A n_B} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_A n_B} \mathrm{d}p + \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} \mathrm{d}n_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} \mathrm{d}n_B \qquad \text{….(2.50)}$$

From the previous unit you will recall that

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_A,n_B} = -S \quad \left(\frac{\partial G}{\partial p}\right)_{T,n_A,n_B} = V \qquad \text{….(2.51)}$$

And by using Eq. (2.48), we can write

$$\left(\frac{\partial G}{\partial n_A}\right)_{T,n_A,n_B} = \mu_A \quad \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} = \mu_B \qquad \text{….(2.52)}$$

Therefore, Eq. (2.50) can be written in the short form as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B \qquad \text{...(2.53)}$$

At constant temperature and pressure, d$T$ = 0 and d$p$= 0, therefore, Eq. (2.53) can be written as

$$\mathrm{d}G = \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B \qquad ...(2.54)$$

This expression gives the change in Gibbs energy with the change in the composition of a binary mixture at constant temperature and pressure. Using Eq. (2.28) and replacing $X$ by $G$, the total Gibbs energy of a binary mixture can be given as follows

$$G = \mu_A n_A + \mu_B n_B \qquad …(2.55)$$

This gives the total Gibbs energy of a binary mixture at a fixed temperature, pressure and composition. For a pure component, Eq. (2.55) can be written as

$$G = \mu_A n_A \qquad …(2.56)$$

Rearranging, we get

$$\Rightarrow \mu_A = \frac{G}{n_A}. \qquad …(2.57)$$

This expression implies that chemical potential of a pure substance is equal to the molar Gibbs energy of that substance. Let us learn about the significance of Chemical potential.

### 2.4.1 Significance of Chemical Potential

The chemical potential of a pure substance is same as the molar Gibbs energy of the substance. The chemical potentials of the pure substances can be compared to determine the relative stability of the substances at a given temperature and pressure. Lower is the value of chemical potential more stable is the substance. Chemical potential plays a significant role in thermodynamic studies of system of variable composition. Therefore, chemical potential can be applied to study a wide range of systems.

The significance of chemical potential is similar to the potential in physics. The system tends to move spontaneously from a higher chemical potential to lower chemical potential state. When two systems are at equilibrium, this means that their temperature, pressure, and chemical potential are equal. Therefore, chemical potential is also used in studying chemical equilibrium and phase equilibrium.

**Chemical Potential: A Physical Insight**

The chemical potential can be seen as ‘escaping tendency’ of a substance in a mixture. The molecules of a component spontaneously move from regions of high chemical potential to the regions of low chemical potential in a mixture. This continues till the chemical potential of the component becomes same throughout the system. For example, if we add a drop of ink in some water taken in a beaker then the molecules of ink in the region of drop gradually but spontaneously spread out. There is a concentration gradient and the molecules at higher chemical potential move spontaneously to the regions of low chemical potential i.e., they diffuse.

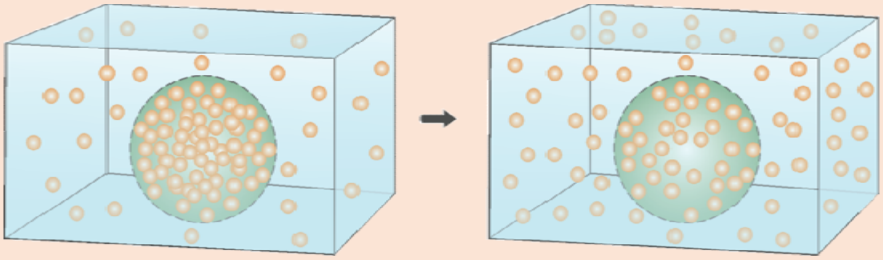


**Fig. 2.3: Schematic representation of a concentration gradient.**

Fig. (2.3) gives a schematic representation of a concentration gradient. The species inside the porous membrane (at higher chemical potential) diffuse out to the region of lower chemical potential outside the membrane. The process continues till the concentrations become equal throughout the system.

The temperature dependence of chemical potential (discussed in next sub section) helps us in understanding how the phase of the system will change under different temperature and pressure conditions. For pure substances, these relations can also predict whether a given substance can exist in solid, liquid, or gaseous state under certain conditions of temperature and pressure. The concept of chemical potential is used to derive the expressions for colligative properties, equilibrium constants and other thermodynamic properties of the system. Chemical potential expressions of half cells are used to derive the Nernst equations of the Galvanic cells.

## 2.4.2 Effect of Temperature and Pressure on Chemical Potential

As seen above, the Chemical potential is a fundamental thermodynamic property that provides an insight into the behaviour of chemical systems. Since chemical potential plays a crucial role in determining the conditions for chemical equilibrium viz., the chemical potentials of reactants and products must be equal. Studying the temperature and pressure dependence of chemical potential helps in predicting the conditions under which chemical reactions will reach equilibrium.

Further, an understanding of temperature and pressure dependence of Chemical potential, can help us gain a deeper understanding of the thermodynamic stability and behaviour of substances. This aspect of chemical potential is particularly relevant to the fields like geology where it helps in explaining geological processes. In environmental science it helps us understand the behaviour of fluids in subsurface reservoirs; the movement of contaminants in the environment etc. let us take up the effect of temperature on chemical potential.

**Effect of temperature on chemical potential**

To study the effect of temperature change on chemical potential for a system we need to differentiate the expression for chemical potential with respect to temperature. You will recall the expression for chemical potential from above,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad \ldots(2.48)$$

Euler's theorem of exactness

A brief to come

Differentiating the expression with respect to temperature keeping pressure and composition constant we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_j} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}\right]_{p,n_i,n_j} \qquad \ldots(2.58)$$

According to Euler's theorem of exactness

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j}\right]_{p,n_i,n_j} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial T}\right)_{p,n_i,n_j}\right]_{T,p,n_j} \qquad \ldots(2.59)$$

We know that,

$$\left(\frac{\partial G}{\partial n_i}\right)_{p,n_i,n_j} = -S$$

Therefore,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_j} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}\right]_{p,n_in_j} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial n_i}\right)_{p,n_in_j}\right]_{T,p,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j} \qquad \ldots(2.60)$$

From the definition of partial molar properties, Eq. (2.13) we can write,

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j} = S_{i,m} \qquad \ldots(2.61)$$

$$\Rightarrow \left(\frac{\partial u_i}{\partial T}\right)_{p,n_i,n_j} = -S_{i,m} \qquad \ldots(2.62)$$

As you know that absolute entropy is always positive, therefore, partial molar entropy also has a positive value. The Eq. (2.62) indicates that $\left(\frac{\partial u_i}{\partial T}\right)_{p,n_i,n_j}$ is always negative. It is clear from these relations that chemical potential will decrease with the increase in temperature. On rearranging Eq. (2.62), we get

$$\mathrm{d}\mu_i = -S_{i,m} dT \qquad \ldots(2.63)$$

On integrating between the limits of temperature, we get

$$\int_{\mu_i(T_1)}^{\mu_i(T_2)} \mathrm{d}\mu_i = \int_{T_1}^{T_2} -S_{i,m}\mathrm{d}T \qquad \ldots(2.64)$$

Simplifying,

$$\mu_i(T_2,p) - \mu_i(T_1,p) = \int_{T_1}^{T_2} -S_{i,m}\mathrm{d}T \qquad \ldots(2.65)$$

The extent of change in chemical potential with temperature will depend upon the partial molar entropy of the component. For a pure substance, the extent of change in chemical potential with temperature will depend upon the molar entropy of that substance. You know that the molar entropy of a substance in vapour phase is maximum and in solid phase is minimum, that is,

$$S_{V,m} >> S_{l,m} > S_{s,m} \qquad \ldots(2.66)$$

Thus, with the increase in temperature, the entropy of the substance will decrease the most if the substance is in the gaseous state. This expression is particularly useful in explaining the colligative properties like, depression in freezing point and elevation in boiling point.

**Effect of pressure change on chemical potential**

As for temperature change, to understand the effect of pressure on chemical potential we differentiate Eq. (2.48) with respect to pressure keeping temperature and composition constant, i.e.,

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i,n_j} = \frac{\partial}{\partial p}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}\right]_{T,n_i,n_j} \qquad \ldots(2.67)$$

According to Euler's theorem of exactness

$$\frac{\partial}{\partial p}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,n_i,n_j}\right]_{T,n_i,n_j} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial p}\right)_{T,n_i,n_j}\right]_{T,p,n_j} = V_{i,m} \qquad \ldots(2.68)$$

Therefore, the expression becomes

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i,n_j} = V_{i,m} \qquad \ldots(2.69)$$

The above equation can be written as

$$\mathrm{d}\mu_i = V_{i,m}\mathrm{d}p \qquad \ldots(2.70)$$

It implies that the chemical potential increases with an increase in the pressure. The extent of increase in the chemical potential for a given increase in pressure will depend upon the value of partial molar volume.

## 2.5 MIXTURE OF GASES

As you have studied above, the chemical potential of a pure substance is same as its molar Gibbs energy. Further, you would recall from previous unit that Gibbs energy change for a pure substance is written as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \qquad \ldots(2.67)$$

Using Eq. (2.63) and Eq. (2.70) we can write the Eq. (2.67) as

$$\mathrm{d}\mu_i = -S_{im}\mathrm{d}T + V_{im}\mathrm{d}p$$

For a pure substance at constant temperature, the above equation becomes

$$\mathrm{d}\mu = V_m\mathrm{d}p \qquad \ldots(2.71)$$

This expression can be integrated to get the chemical potential values for different pressures at a given temperature.

$$\int_{\mu(T,p_1)}^{\mu(T,p_2)} \mathrm{d}\mu_i = \int_{p_1}^{p_2} V_m \mathrm{d}p \qquad \ldots(2.72)$$

However, since the molar volume is pressure dependent the integration of right side is not straight forward. In the case of solids and liquids, they are not easily compressed, so for small pressure range the molar volume of a pure solid or a pure liquid substance can be assumed to be constant. In such cases, the molar volume term can be taken out of the integral.

Therefore, for pure solid and pure liquid

$$\int_{\mu(T,p_1)}^{\mu(T,p_2)} \mathrm{d}\mu = V_m \int_{p_1}^{p_2} \mathrm{d}p \qquad \ldots(2.73)$$

If $p_1$is taken as standard pressure (1 bar), then the chemical potential at 1 bar is the standard chemical potential of the substance, $\mu^o$. Therefore, the chemical potential at any other pressure, $p$ is written as

$$\mu(T,p) = \mu^o(T) = V_m(p-1) \qquad \ldots(2.74)$$

**Chemical potential of an ideal gas in terms of pressure**

Now let us take the case of gases. In this case the molar volume changes with the change in pressure. So, for gases we have to write molar volume in terms of pressure. There are different equations of state which relate molar volume with pressure. We will take the ideal gas equation.

For an ideal gas $V_m = \frac{RT}{p}$ …(2.75)

Therefore, Eq. (2.72) can be written as

$$\int_{\mu(T,p_1)}^{\mu(T,p_2)} \mathrm{d}\mu = \int_{p_1}^{p_2} \frac{RT}{p} \mathrm{d}p \qquad \ldots(2.76)$$

Integrating between the limits, we get

$$\mu(T,p_2) - \mu(T,p_1) = RT \int_{p_1}^{p_2} \mathrm{d}\ln p \qquad \ldots(2.77)$$

For initial pressure ($p^o$)equal to 1 bar, the chemical potential is equal to the standard chemical potential of the gas, the equation becomes

$$\mu(T,p) - \mu^0(T) = RT \ln\left(\frac{p}{p^0}\right) \qquad \ldots(2.78)$$

Since $p^o$ is 1 bar, the equation is written as

$$\mu(T,p) - \mu^0(T) = RT \ln p \qquad \ldots(2.79)$$

As can be seen from the above expression, the chemical potential of an ideal gas increases with the increase in pressure. If the standard chemical potential of an ideal gas is known at a given temperature, then the chemical potential can be calculated at any other pressure and given temperature. Remember that standard conditions do not include the temperature. Hence, standard chemical potential at different temperatures will be different. Wherever the temperature is not mentioned for the standard values, it is taken as 298 K.

You know that the gases move from high pressure region to low pressure region. Now let us state the same fact in terms of chemical potential. At high pressure, chemical potential is more as compared to the chemical potential at lower pressure. Hence, gases move spontaneously from higher chemical potential state to the lower chemical potential state. Therefore, chemical potential is also a measure of escaping tendency of the gas (recall the physical insight on chemical potential, given above).

### Chemical potential of a real gas in terms of fugacity

The Eq. (2.78) gives the chemical potential of an ideal gas. However, a real gas is expected to have a different behaviour depending upon the size of its molecules and intermolecular interactions present in it. You have studied various equations of state for real gases in your earlier classes. However, these equations show deviations under certain conditions of temperature and pressure. Writing different equations of state under different conditions makes the expression complicated. To simplify things, in the case of real gases, pressure is replaced by the term *fugacity* (*f*). All the deviations arising due to intermolecular interactions are included in it. Therefore, it is known as corrected pressure, and it has the unit of pressure.

$$f = \gamma p \qquad \ldots(2.80)$$

Here, $\gamma$ is known as fugacity coefficient. Its value is equal to 1 for an ideal gas. At very low pressures, fugacity coefficient can be approximately taken as 1 for real gases. That is, $\lim_{p \to 0} \gamma \to 1$.

For real gases, Eq. (2.78) is modified as

$$\mu(T,p) - \mu^0(T) = RT \ln\left(\frac{f}{p^0}\right) = RT\, ln\left(\frac{\gamma p}{p^0}\right) \qquad \ldots(2.81)$$

Since $p^\circ = 1\,\text{bar}$, the equation is written as

$$\mu(T,p) - \mu^0(T) = RT \ln p \text{ - } RT \ln \gamma \qquad \ldots(2.82)$$

If we compare Eq. (2.78) for ideal gases and Eq. (2.82) for the real gaseswe find that there is an addition term, viz., $RT \ln \gamma$. This term accounts for all the deviations from ideal behaviour.

### Chemical potential of an ideal gas in a mixture of ideal gases

Whenever two or more gases are present in a system it is known as a mixture of gases. During the study of thermodynamic properties of the gaseous mixture, it is easier to assume that all the components of the mixture are ideal gases. The thermodynamic expressions obtained for a mixture of ideal gases can then be further modified to get the expressions for the mixture of real gases.

It is assumed that when the gases are mixed then the temperature and the total pressure are fixed. So, what happens when the gases are mixed and how do the thermodynamic property of the mixture differ from the thermodynamic properties of the pure components.

Recall that in a mixture of gases, the contribution of each gas to the total pressure of the mixture ($p$) is known as the partial pressure of that component ($p_i$) and it depends upon the mole fraction of the component ($x_i$) in the mixture as stated by Dalton's law of partial pressures.

$$p_i = x_i p \qquad \ldots(2.83)$$

Let us find how the chemical potential changes when a pure ideal gas is added to the mixture of ideal gases. The change in chemical potential of a component at constant temperature is given by the expression

$$d\mu_i = V_{i,m} dp \qquad \ldots(2.84)$$

For ideal gas, since the partial molar volume is equal to its molar volume, $V_{i,m} = RT / p$. Therefore, the expression for $d\mu_i$ is written as

$$d\mu_i = \frac{RT}{p} dp = RTd \ln p \qquad \ldots(2.85)$$

To find the total change in the chemical potential on mixing, we have to integrate the above equation. Let us take the initial state as pure gas at the pressure of 1 bar, that is the standard pressure ($p^o$) and any temperature $T$. The chemical potential under these conditions is equal to the standard chemical potential of the pure component $\mu_i^\circ$. The final state is the gas in the mixture at temperature $T$ and partial pressure $p_i$. Let the chemical potential of the component in the mixture be $\mu_i$. Upon integrating the expression, we get,

$$\int_{\mu_i^0(T)}^{\mu_i(T)} d\mu = RT \int_{p^0}^{p_i} d \ln dp \qquad \ldots(2.86)$$

$$\mu_i(T) = \mu_i^0(T) = RT \ln \frac{p_i}{p^0} \qquad \ldots(2.87)$$

Since the partial pressure of a gas is always less than the pressure of pure gas, the right hand side of the above equation is negative. Thus,it can be seen from Eq. (2.87) that the chemical potential of an ideal gas is less in a mixture as compared to the pure gas. Since, there is a decrease in the chemical potential of the gas on mixing, the mixing of the ideal gases is a spontaneous process.

## 2.6 GIBBS-DUHEM EQUATION

As shown earlier, the change in the extensive property $X$ at constant temperature and pressure is given by Eq.(2.24)

$$\mathrm{d}X = X_{m,A} \mathrm{d}n_A + X_{m,B} \mathrm{d}n_B \qquad \ldots(2.24)$$

Whereas, the total extensive property at a given temperature, pressure and composition is given by Eq.(2.28)

$$X = X_{m,A}n_A + X_{m,B}n_B \quad \text{…(2.28)}$$

The differential form of Eq.(2.28) will give the total change in $X$ as

$$\mathrm{d}X = X_{m,A}\mathrm{d}n_A + n_A\mathrm{d}X_{m,A} + X_{m,B}\mathrm{d}n_B + n_B\mathrm{d}X_{m,B} \quad \text{...(2.88)}$$

Since, both Eqs. (2.28) and (2.88) represent total change in the state variable $X$, the equations are equal. Therefore,

$$X_{m,A}n_A + X_{m,B}n_B = X_{m,A}\mathrm{d}n_A + n_A\mathrm{d}X_{m,A} + X_{m,B}\mathrm{d}n_B + n_B\mathrm{d}X_{m,B} \quad \text{…(2.89)}$$

Simplifying, we get

$$n_A\mathrm{d}X_{m,A} + n_B\mathrm{d}X_{m,B} = 0 \quad \text{...(2.90)}$$

The Eq. (2.90) is the general form of a very important relation which is known as *Gibbs-Duhem equation.*

Gibbs-Duhem equation can be written in terms of volume as

$$n_A\mathrm{d}V_{m,A} + n_B\mathrm{d}V_{m,B} = 0$$

or

$$n_A\mathrm{d}V_{m,A} = -n_B\mathrm{d}V_{m,B} \quad \text{...(2.91)}$$

This relation implies that for a binary system, the partial molar volume of a component cannot change independent of the partial molar volume of the other component. If partial molar volume of a given component is increased by some method, then the partial molar volume of the second component will decrease.

This is true for all the types of partial molar quantities. The Gibbs-Duhem equation in terms of chemical potential is written as

$$n_A\mathrm{d}\mu_A + n_B\mathrm{d}\mu_B = 0 \quad \text{...(2.92)}$$

If the changes in temperature and pressure are also considered, then the Gibbs-Duhem equation in terms of chemical potential is written as

$$-S\mathrm{d}T + V\mathrm{d}p + n_A\mathrm{d}\mu_A + n_B\mathrm{d}\mu_B = 0 \quad \text{...(2.93)}$$

## *SAQ 5*

For a binary mixture in which $n_A = 3n_B$ if the chemical potential of A changes by 2 J mol$^{-1}$ what is the change in the chemical potential of B?

## *SAQ 6*

In a binary mixture of ideal gases in which $n_A = 5n_B$, the partial molar volume of B was decreased by 0.01 m$^3$ mol$^{-1}$. What would be the change in the partial molar volume of A?

## 2.7 SUMMARY

In this unit, we have discussed about the issue of the effect of change in composition of the system on its thermodynamic properties. We began the unit by initiating a discussion on partial molar properties and attempting to understand their significance. Herein, we briefly recalled the expressions like, molarity, molality and mole fraction commonly used to express the composition of a given system. Thereafter, we first defined molar properties as the thermodynamic property per mole of the system. We stated that the thermodynamic properties of a system of variable composition is a function of the pressure, temperature, and the composition of the system. The change in each one of these causes a change in the property and the total change in the property is equal to the sum of these changes. The partial molar property of component A in a mixture has been defined as the change in the property X of the mixture when one mole of component A is added to a large volume of mixture at constant temperature & pressure while keeping the amountsof remaining components constant. Having defined partial molar properties, we developed the relationship between the thermodynamic properties and the corresponding partial molar properties.

We then took up a specific partial molar property viz., partial molar volume as it is easier to visualise the changes. We defined partial molar volume and provided an insight into its physical meaning using an example and explained its experimental determination. Thereafter, we took up an important quantity viz., chemical potential i.e., Gibbs energy per mole. We discussed the effect of pressure and temperature on this fundamental property. It has the same significance in systems with variable composition as Gibbs energy has for pure components. We then took up systems consisting of mixtures of gases. In this context we brought in the concept of fugacity and explain its significance. Towards the end of the unit, we derived Gibbs-Duhem equation and explained that it states that partial molar properties of various components in a mixture cannot be changed independent of each other.

## 2.8 TERMINAL QUESTIONS

1. Define partial molar property.
2. Calculate the partial molar volume of water in an equimolar mixture of ethanol and water for which the partial molar volume of ethanol is found to be 57.4 $cm^3 mol^{-1}$. Given that the density of the mixture is 0.80 $g cm^{-3}$.
3. Define chemical potential. How will the chemical potential of an ideal gas change if the pressure of the gas is increased at constant temperature.
4. Show that for an ideal gas in a mixture, the partial molar volume is equal to *RT/p.*
5. Show that in a binary mixture when the chemical potential of component A decreases then the chemical potential of component B will increase if the temperature and pressure are fixed.

# 2.9 ANSWERS

## Self-Assessment Questions

1. i) We are given a solution containing 6.30 g of oxalic acid per 100 $cm^3$ of the solution.

We know that molarity ($c_i$) of a solution is given as.

$$c_i = \frac{n_i \times 1000}{V} \text{ mol dm}^{-3}$$

Now $n_i$ = 6.30 g /126 g $mol^{-1}$= 0.05 mol ; V= 100 $cm^3$

Substituting, we get

$$c_i = \frac{0.05 \times 1000}{100} = 0.5$$

ii) We are given a solution containing 6.30 g of oxalic acid per 100 g of water

We know that molality ( $m_i$ ) of a solution is given as.

$$m_i = \frac{n_i \times 1000}{w} \text{ mol kg}^{-1}$$

We have calculated $n_i$ as 0.05;w= 100g (Given)

Substituting, we get

$$m_i = \frac{n_i \times 1000}{w} = 0.05 \times 1000 /100=0.5$$

2. i) Given: mass of ethanol = 23 g. mass of water 180 g.
We know that the mole fraction is given as

$$\chi_i = \frac{n_i}{n_{total}}$$

Mole fraction of ethanol $x_e = \frac{n_e}{n_e + n_w}$

➔ number of moles of ethanol $= n_e = \frac{23\,g}{46\,g\,mol^{-1}} = 0.5\,mol$

number of moles of water $= n_w = \frac{180\,g}{18\,g\,mol^{-1}} = 10\,mol$

$$x_e = \frac{0.5}{0.5+10} = 0.0476$$

ii) $n_e = \frac{100\,g}{46\,g\,mol^{-1}} = 2.17\,mol$

$$n_w = \frac{18\,g}{18\,g\,mol^{-1}} = 1.0\,mol$$

$$x_e = \frac{2.17}{2.17+1.0} = 0.685$$

3. The partial molar properties are relevant only for extensive thermodynamic properties and we know that temperature is an intensive property. Further, the temperature of a system will not change by changing composition of the system. Therefore, partial molar temperature for a mixture is irrelevant.

4. According to Eq. (2.34) we can write, the expression for total volume as

   $$V = V_{m,w} n_w + V_{m,e} n_e$$

   We are given: $n_w$ = 2.0 mol & $n_e$ = 2.0 mol

   Thus, the mole fraction of ethanol = $\dfrac{2\text{ mol}}{2\text{ mol} + 2\,\text{mol}} = 0.5$

   Now for the mole fraction equal to 0.5 the partial molar volumes are given as

   Partial molar volume of water, $V_{m,w}$ = 16.9 $\text{cm}^3\ \text{mol}^{-1}$

   Partial molar volume of ethanol, $V_{m,e}$ = 57.4 $\text{cm}^3\ \text{mol}^{-1}$

   Substituting the values in the expression for total volume, we get

   $$V = (16.9\,\text{cm}^3\ \text{mol}^{-1} \times 2.0\,\text{mol}) + (57.4\,\text{cm}^3\ \text{mol}^{-1} \times 2.0\,\text{mol}) = 148.6\,\text{cm}^3$$

   Thus, the volume of the solution would be = $148.6\,\text{cm}^3$.

5. According to Gibbs-Duhem equation

   $$n_A \text{d}\mu_A + n_B \text{d}\mu_B = 0$$

   $$n_A = 3n_B, \text{d}\mu_A = 2\,\text{J}\text{mol}^{-1}$$

   $$\text{d}\mu_B = -\frac{n_A}{n_B}\text{d}\mu_A = -\frac{3n_B}{n_B} \times 2\,\text{J}\text{mol}^{-1} = -6\,\text{J}\text{mol}^{-1}$$

6. According to Gibbs-Duhem equation $n_A \text{d}V_{A,m} = -n_B \text{d}V_{B,m}$

   $$n_A 5n_B,\ V_{B,m} = -0.01\text{m}^3\ \text{mol}^{-1}$$

   $$\text{d}V_{A,m} = -\frac{n_B}{n_A}\text{d}V_{B,m} = -\frac{n_B}{5n_B} \times (-0.01)\text{m}^3\text{mol}^{-1} = 0.002\,\text{m}^3\ \text{mol}^{-1}$$

   Partial molar volume of A increases by 0.002 $\text{m}^3\ \text{mol}^{-1}$

## Terminal Questions

1. Partial molar property gives the change in thermodynamic property of the mixture if one mole of a component is added to the mixture at constant temperature, pressure and keeping the amount of the rest of the components constant. For any thermodynamic property *X,* partial molar property of component *i* is written as $\left(\dfrac{\partial X}{\partial n_i}\right)_{T,p,n_j}$

2. Let us assume the partial molar volumes of ethanol and water to be $V_{m,e}$ and $V_{m,w}$ respectively

   Given: $V_{m,e} = 57.4\,\text{cm}^3\text{mol}^{-1}$ and $V_{m,w} = ?$

   Using Eq. (2.34) we can write, the expression for total volume as

   $V = V_{m,e}n_e + V_{m,w}n_w$

   We know that $M_e = 46.4\,\text{gmol}^{-1}$ & $M_w = 18.0\,\text{gmol}^{-1}$

   Given: $\chi_e = 0.5$ & $\chi_w = 0.5$

   Therefore, the molar mass of the equimolar mixture of ethanol and water can be estimated as

   $$M = M_e\chi_e + M_w\chi_w$$
   $$= [46.4\,\text{gmol}^{-1} \times 0.5] + [18.0\,\text{gmol}^{-1} \times 0.5] = 32\ \text{gmol}^{-1}$$

   Molar volume of the mixture is given by

   $$V_m = \frac{\text{Mass}}{\text{Density}} = \frac{32\ \text{g mol}^{-1}}{0.8002\ \text{gcm}^{-3}} = 39.99\ \text{gmol}^{-1}$$

   We know that the molar volume of the mixture, $V = V_{m,w}n_w + V_{m,e}n_e$

   Substituting

   $$39.99 = (0.5 \times 57.4) + (0.5 \times V_{m,w})$$

   Solving, $V_{m,w} = \dfrac{(39.99 - 28.70)}{0.5} = 22.58\ \text{gcm}^{-3}$

   Hence, the partial molar of water in the given mixture, $V_{m,w} = 22.58\ \text{gcm}^{-3}$

3. Chemical potential is equal to partial molar Gibbs energy. For any component *i,* the chemical potential is written as $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,p,n_j}$

   The variation of chemical potential with pressure for an ideal gas is given by the expression $d\mu_i = \dfrac{RT}{p}dp$. Therefore, as the pressure increases, chemical potential of the gas will also increase.

4. Partial molar volume is equal to $\left(\dfrac{\partial V}{\partial n_i}\right)_{T,p,n_j}$. For an ideal gas $V = nRT/p$.

   $n = n_1 + n_2 + n_3 + \ldots.$ $n = n_1 + n_2 + n_3 + \ldots.$

   $$V = \frac{RT}{p}(n_1 + n_2 + n_3 + \ldots)$$

   Therefore, $\left(\dfrac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \dfrac{RT}{p}$. This will be same for all the ideal gases in the mixture.

5. In a binary mixture at constant temperature and pressure

$$\mathrm{d}G = \mu_{m,A}\mathrm{d}n_A + \mu_{m,B}\mathrm{d}n_B \qquad ...(A)$$

We know that at constant temperature and pressure $\mathrm{d}G = \mu_{m,A}n_A + \mu_{m,B}n_B$

$$\mathrm{d}G = \mu_{m,A}\mathrm{d}n_A + \mu_{m,B}\mathrm{d}n_B + n_A\mathrm{d}\mu_{m,A} + n_B\mathrm{d}\mu_{m,B} \qquad ...(B)$$

Comparing right hand sides of Eqs (A) and (B) we get

$$n_A\mathrm{d}\mu_{m,A} + n_B\mathrm{d}\mu_{m,B} = 0 \text{ or } n_A\mathrm{d}\mu_{m,A} = -n_B\mathrm{d}\mu_{m,B}$$

It can be seen from the above equation that as chemical potential of one component increases, the chemical potential of the second component will decrease.

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# UNIT 3

# INTRODUCTION TO STATISTICAL THERMODYNAMICS-I

## Structure

3.1 Introduction
Expected Learning Outcomes
3.2 Classical vs Statistical Thermodynamics
3.3 Basic Probability Theory
Permutations and Configurations
Stirling Approximation
3.4 Probability Distribution functions
3.5 Summary
3.6 Terminal Questions
3.7 Answers

## 3.1 INTRODUCTION

You know that thermodynamics refers to the study of heat and its relation to other forms of energy. The term ‘thermodynamics’ was coined by Lord Kelvin (1824-1907) to signify the dynamic nature of heat, which was then considered to be a kind of fluid. If we take literal translation, thermodynamics conveys the dynamics (or motion) of heat. In your earlier classes you have learnt about thermodynamics from a phenomenological perspective wherein the observation of macroscopic phenomenon is expressed in terms of mathematical relationships. The generalities emanating from the extensive observation of macroscopic world over hundreds of years are stated in terms of the laws of thermodynamics. These laws are applicable to all macroscopic systems, irrespective of their physical state, whether solid, liquid, gas, or any combination of these states. These laws have withstood the test of time and have proved quite useful in understanding / determining the thermodynamic properties of a system.

In this and the next unit we will introduce you to an alternative approach to understand thermodynamic properties of a system. It is based on the application of statistics to large collections of microscopic systems like atoms and molecules. In fact, it provides the link between the microscopic

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perspective of matter (the quantised energy levels at the atomic / molecular level) and its macroscopic or bulk (observable) properties. This approach can be used to calculate the bulk thermodynamic properties such as internal energy, enthalpy, entropy, and Gibbs energy of the system from structural and spectroscopic data of microscopic systems constituting the thermodynamic system. It is important to note that though quantum mechanics is at the foundation of statistical thermodynamics, we need not have the knowledge of the intricate details of quantum mechanics. Merely the basic ideas of energy levels, energy states, and intermolecular forces are sufficient to develop a satisfactory theory.

In a way, Statistical thermodynamics can be considered as a mathematical tool that bridges the gap between the properties of individual molecules in a system and the macroscopic thermodynamic properties of the bulk matter. Alternatively, statistical thermodynamics can be visualised as a vehicle that serves to provide means to extend the properties of individual atoms and molecules to a large collection of them.

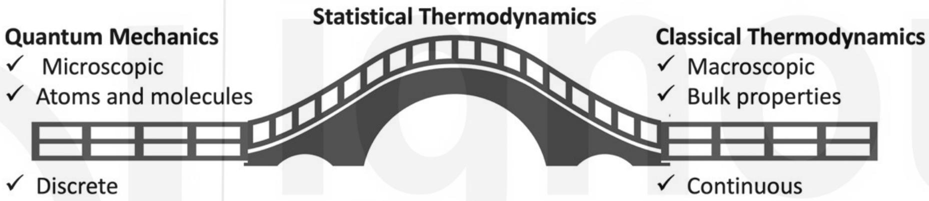


**Fig. 1.1: Schematic representation of statistical thermodynamics being a bridge between quantum mechanics and classical thermodynamics.**

We will begin the unit by delineating the relationship between classical and statistical thermodynamics. This will be followed by a discussion on basic probability theory. Herein, we will introduce the concept of probability and explain the meaning of permutations and configurations with the help of suitable examples. This will be followed by introducing an important approximation i.e., Stirling approximation. We will discuss the need for and importance of this approximation. Then we will take up the probability distribution functions and learn about their characteristics.

In the next unit we will continue with the discussion on statistical thermodynamics.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- discuss the relationship between classical and statistical thermodynamics;
- explain the basic terms related to probability theory;
- calculate the probability of randomised experiments;
- explain the difference between permutation and configuration;
- calculate the permutations and configurations for systems with small number of objects;

- state Stirling's approximation and outline its significance;
- establish the validity of Stirling's approximation for systems with large number of particles;
- define and classify probability distribution functions; and
- outline the characteristics of probability distribution functions.

## 3.2 CLASSICAL VERSUS STATISTICAL THERMODYNAMICS

In any chemical system we deal with many molecules e.g., a sample of one mole of a hydrogen gas contains as many as $6.022 \times 10^{23}$ molecules of hydrogen. The experimentally determined macroscopic properties of the system, correspond to a kind of an average of the molecular properties. In your earlier study of thermodynamics, you would have calculated the macroscopic properties of the system without paying attention to the properties of the individual molecules. On the other hand, in quantum mechanics, you had studied the properties of a single atom / molecule. This was done by solving the Schrodinger wave equation to calculate the different energy states available in a molecule. You would recall that the quantised energy states for a molecule include translational, electronic, rotational, and vibrational energy states. These all contribute to the total energy of the molecule. These discrete energy states are represented in terms of an energy expression and are identified by the respective quantum numbers.

You may argue that if we know the energy of one molecule, then we can calculate the total energy of one mole of these molecules simply by multiplying the energy of the single molecule by Avogadro's constant. This simplified view could be applicable if all the molecules in the sample had equal energies, but it is not so. To understand this let us consider an ideal gas at equilibrium i.e., the total energy of the gas does not change with time. Now, since the individual molecules are in a constant state of random motion and keep colliding with each other, some molecules will gain momentum and others will lose it during these collisions. Therefore, the kinetic energy of individual molecules will not be same i.e., the energies are distributed over a range. Recall, that you have already studied this while discussing the Maxwell distribution of velocity in the kinetic theory of gases.

Besides the kinetic energy, we also know that there are various rotational and vibrational energy states available which the molecules can occupy. Though under low temperature conditions all the molecules may have same ground state electronic energy, they may still have different translational, rotational, and vibrational energies i.e., these molecules will be occupying vibrational and rotational states of different energy. Thus, we can say that the total energy is not equally distributed among the molecules. There are different combinations of energy states which the molecules can occupy in such a way that the total energy of the system remains constant. The statistical treatment of such systems allows us to calculate the fraction of molecules that occupy a given energy state. Once we know the fractions of the molecules occupying different energy states, we can estimate the macroscopic properties of the system. In

In a macroscopic system the molecules are distributed over many available energy states at the microscopic level.

other words, the properties of the individual molecules are scaled to macroscopic level using theory of probability and suitable statistical tools. In the next unit we will study how the macroscopic properties of a system can be calculated from the properties of a single particle using the concept of statistics.

We can say that both the approaches to the understanding of thermodynamic systems are based on experimental data, however the type of data involved in the two cases is different. The classical thermodynamics uses the data based on the bulk properties of matter i.e., density, pressure, heat capacity etc. whereas the statistical thermodynamics uses the molecular properties like, bond lengths, quantised energies, vibration frequencies etc. As an example, the experimental value of enthalpy of formation of $H_2O(g)$ is -241.8 kJ $mol^{-1}$at 298 K and 1atm. It refers to the enthalpy change associated with the formation of one mole of water vapours from its constituent elements in their standard states under standard conditions. Classically speaking it has nothing to do with the microscopic nature of the species involved and what determines the observed value. On the other hand, the statistical thermodynamics, deals with what in the individual atoms and molecules determines the observed value.

In conclusion we can say that the classical thermodynamics ignores molecular complexity i.e., the quantum mechanical nature of the molecules whereas the statistical thermodynamics deals primarily with the quantum mechanical nature of atoms and molecules. As stated above, statistical thermodynamics represents a probabilistic approach to study the thermodynamic systems. Therefore, a basic understanding of probability and related concepts is a must to learn the statistical approach to thermodynamics. Let us learn about the same. However, before that answer the following simple question to assess your understanding.

*SAQ 1*

Statistical mechanics provides a theoretical basis for the experimental science of thermodynamics. Comment.

## 3.3 BASIC PROBABILITY THEORY

You might have learnt about the term, ‘probability’ in your earlier classes or maybe you are aware of it otherwise. The probability refers to the likelihood of a given event to occur. The outcome of an experiment is represented in terms of a random variable (X). The same experiment on being repeated many times can give rise to (slightly) different values which can be discrete or continuous. For example, when we throw a die, the random variable is the number of dots on the top face of the dice; it has discrete values.

If an experiment can have more than one outcome, then probability refers to the chances of getting a particular (desired) outcome. The most common example of using probability is in tossing of a coin. A coin has two faces, head, and tail. In an experiment involving, tossing of an unbiased (fair) coin, the outcome can be either a head or a tail. Head and tail are referred to as the possible **events** or **outcomes** of tossing a coin. The probability of getting a head is mathematically written as

$$p(H) = P(H) = P_H = \frac{1}{2} \qquad \dots(3.1)$$

Thus, there is 50% chance of getting a head and 50% chance of getting a tail in a throw of the coin. The total probability of all the events / outcomes in an experiment is always equal to one.

$$p(H) + p(T) = \frac{1}{2} + \frac{1}{2} = 1 \qquad \dots(3.2)$$

If two coins are tossed simultaneously, then the possible outcomes will be:

| **First coin** | H | H | T | T |
|---|---|---|---|---|
| **Second coin** | H | T | H | T |

The collection of all possible outcomes of an experiment is known as the sample space.An **event** refers to any outcome or collection of outcomes in the sample space and may include the null set as well as the set of all possible outcomes. For example,the sample space for tossing two coins has four events or outcomes, i.e., HH, TT, HT, and TH. These constitute the sample space for the experiment.

Let us take an example of travelling from city A to city C via city B. If there are X ways of reaching city B from city A and Y ways of going from city B to city C then the total number of ways one can go from city A to city C will be X.Y. Therefore, the sample space for the event (going from city A to city C) will consists of all the X.Y elements. You may note here that in probability an event may consist of a series of actions, so the sample space consists of all possible outcomes.

If the sample space has N mutually exclusive events and an event of interest (A) occurs $I$ times, then the probability of that event is given as

$$P(A) = \frac{I}{N} \qquad \dots(3.3)$$

For $N$ mutually exclusive, equally likely points in sample space, if $I$ of these correspond to the random event A, then the probability $P(A) = \frac{I}{N}$

Therefore, the probability of the event of getting one head and one tail i.e., P(HT) = 2/4 = ½. In this case, the event is getting one head and one tail and includes two elements of the sample space i.e., it refers to the following subset [HT, TH] of the sample space. This example refers to the probability associated with a single experiment of throwing two coins.

Many a times we are interested in the probability of an event, that is, the probability of a specific outcome for a series of experiments. Let us take an example for the calculation of probability for a desired outcome in the repeated tossing of a coin.

**Example 3.1**: Consider an experiment involving tossing a coin four times. Calculate the probability of getting at least two heads in the experiment.

**Solution**: In this case we have a coin that is to be tossed four times. In every toss we have two possible outcomes i.e., a head or a tail. We can write down all the possible outcomes of the experiment as follows:

| Outcome No. | Toss 1 | Toss 2 | Toss 3 | Toss 4 | Outcome No. | Toss 1 | Toss 2 | Toss 3 | Toss 4 |
|---|---|---|---|---|---|---|---|---|---|
| **1** | H | H | H | H | **9** | H | T | T | H |
| **2** | T | H | H | H | **10** | H | T | H | T |
| **3** | H | T | H | H | **11** | H | H | T | T |
| **4** | H | H | T | H | **12** | T | T | T | H |
| **5** | H | H | H | T | **13** | T | T | H | T |
| **6** | T | T | H | H | **14** | T | H | T | T |
| **7** | T | H | T | H | **15** | H | T | T | T |
| **8** | T | H | H | T | **16** | T | T | T | T |

Thus, there are a total of sixteen possible outcomes of the experiment of tossing a coin four times i.e., the sample space has sixteen outcomes.Of the 16 possible outcomes, 11 meet our requirement of having at least two heads. Therefore, the probability of getting at least two heads after tossing a coin four times will be $^{11}\!/_{16}$ i.e., the number of desired outcomes divided by the total number of possible outcomes.

Similarly, when we roll an unloaded dice(the one in which the chance of any**one** of the six faces to be the top face is the same as that of any **other** face), the probability that we get number 6 on the top face is 1/6 as it is one of the six possible outcomes. Similarly, the other numbers from 1 to 5 will have the same probabilities and the sum of all the probabilities will be 1.

$$\frac{1}{6}+\frac{1}{6}+\frac{1}{6}+\frac{1}{6}+\frac{1}{6}+\frac{1}{6}=1 \qquad \text{…(3.4)}$$

Now, we consider a slightly more complex case of rolling a pair of unloaded dice. There is only one outcome in which we get the sum of the numbers on top face to be equal to two i.e., when both dice show 1, such an event is identified as "throws a two". Similarly, there are only two possibilities for "throws a three" i.e., when we get the outcome as (2,1) or (1,2). All the possibilities in the rolling of a pair of dice are as compiled below:

| Outcome (as ‘throws a..’) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number of ways | 1 | 2 | 3 | 4 | 5 | 6 | 5 | 4 | 3 | 2 | 1 | **36** |

The sample space for rolling a pair of dice has a total of 36 outcomes. You may note that in the above example, ‘throwing a seven’ is the most probable event i.e., the one that can be accomplished in the greatest number of ways. Since it can occur in 6 possible ways, it has a probability of 6/36=1/6. You may also note that the six ways of ‘throws a seven’ are [(1,6), (2,5), (3,4), (4,3), (5,2) and (6,1)] and these have been considered as equivalent as in the example of throwing two coins, HT and TH are considered equivalent.

It is important to state that the **random** or **randomised variables**, or quantities are those variables whose value can change throughout the course of an experiment or series of events.In the above examples, the sides of the coin, the number on top face of the dice are the variables that change the outcome of the experiment. The variables can be **discrete variables** i.e., the ones that can have countable number of values. For example, a coin has only 2 sides, so it has only two variables, whereas dice has six variables. In the event of picking one student from a class of 60 students, has 60 variables. It is important to note that the number of outcomes may be astronomical however as long as the possible outcomes are countable it will remain discrete.In case of discrete variables, the sample space is represented as a collection of all the variables. For example, the sample space in the experiment involving throwing a fair dice will be {1,2,3,4,5,6}.

On the other hand, we can have **continuous variables** that can have any value in the given range of values say areal number between 0 and 1 is an example of continuous variable. Contrasting with discrete variables, a continuous variable has uncountable set of possible outcomes.Temperature is another example of continuous variable as the system temperature can be anywhere from zero K onwards. A yet another example could be the distance travelled by different people within a given time interval. In case of continuous variables, the sample space is represented by stating set of limits in which the variable varies i.e., the variable may have any value in a range, say $a \le x \le b$. For example, if the continuous variable can have any value from 1 to 100 it will be represented as $1 \le X \le 100$.

It is pertinent to point out that in the chemical systems we are interested in, the observables are random and fluctuating in nature. For example, the instantaneous vapour pressure of a liquid in equilibrium with its vapour continuously fluctuates around an average value. Similarly, the energy of a system at constant temperature or the volume of a system at constant pressure keeps on fluctuating around an average value. However, the outcome of the measurement may be different from the average value and cannot be predicted. Therefore, we need some kind of probability distribution to describe the behaviour of the random variables. We will take it up towards the end of the unit. Having learnt about important elementary terms related to probability, let us now take up two critical concepts viz., permutations and configurations. However, before that answer the following simple questions to assess your understanding.

## *SAQ 2*

Define sample space. Write the sample space for drawing a queen of heart or diamond from a deck of playing cards.

## *SAQ 3*

Define the term, ‘continuous variable’. If the temperature in the capital city of Delhi varies from 2°C to 46°C. How would you represent the sample space for the temperature in Delhi.

### 3.3.1 Permutations and Combinations

As shown above, to calculate the probability of an event we need to count the total number of events. This is an easy exercise in situations with a small number of events. However, the exercise becomes increasingly difficult when the number of events is large, say simultaneously tossing 100 coins or rolling 20 dice. A much easier way to calculate the total number of outcomes of an experiment is based on the **fundamental counting principle**. According to this principle, if there are $N_1$ ways of doing first thing, $N_2$ ways of doing the second thing, $N_3$ ways of doing third thing and so on, then the total number of possible outcomes is equal to

$$(N_1).(N_2).(N_3)..... \qquad \text{...(3.5)}$$

Let us again calculate the total number of outcomes for rolling a pair of dice by using the fundamental counting principle. For the first dice there are six possible outcomes, similarly for rolling the second diceagain there are six ways. So, the total number of possible outcomes is $6\times6=36$. Similarly, if we roll three dice, the total number of outcomes will be $6\times6\times6 = 216$ and so on i.e., it will be $6^N$ for $N$ dice. It is equivalent to the number of outcomes for drawing $R$ objects from a total of $N$ objects such that firstly the objects are replaced after every pick and secondly the order in which the objects are drawn matters is given by the following expression.

$$\text{Number of permutations} = N^R \qquad \text{... (3.6)}$$

In the examples of tossing two coins, we have considered certain events (e.g., HT and TH) as equivalent, i.e., the order of choosing the variable or object does not affect the total outcomes.

***Permutations***

Let us now count the total number of outcomes when the order of choosing the objects does affect the total number of possible outcomes with the help of some examples.

**Example 3.2**: Consider a box containing four different balls labelled A, B, C and D. Calculate the number of possible ways of randomly selecting the four original balls out of the box without replacement.

**Solution**: The first ball chosen can be any of four available, the second pick can be any of the remaining three balls, the third ball chosen must be one of the two remaining possibilities, and for the fourth there is only one possibility. Hence, the number of ways that the four sequential but independent choices can be made must be $4\times3\times2\times1 = 24$.

These 24 possible ways of randomly selecting the four original balls are the number of possible arrangements or permutations of any single sequence of the four balls, e.g., ABCD.

You may note here that if the balls were not labelled, i.e., these were indistinguishable then the 24 possible arrangements discussed above would refer to only one *combination.* That is, only a single collection or combination of the four balls would exist. Also, if we chose to disregard the ordering of picking the balls then even if the balls are labelled, we will have only one combination. Let us take another example.

**Example 3.3**: Calculate the number of possible unique nine-digit numbers that can be formed by using the digits 1-9 just once in the number.

**Solution**: While writing the desired number, there nine choices (any number from 1-9) available for the first digit. For the second digit only 8 choices are available as one numeral has already been used and cannot be used again. In the similar manner the number of available choices decreases by one for each subsequent digit. Thus, the total possible unique nine-digit numbers will be $9\times8\times7\times6\times5\times4\times3\times2\times1 = 362880 = 9!$

Each number in the example3.3 is made up of unique arrangement of the numerals and is known as *permutation of nine numerals*. Thus, from these examples we say that the **permutation** is a unique arrangement of all the available objects in which the order of selection affects the arrangement. In such type of permutation, all the available objects are used in the arrangement. The number of permutations for drawing $N$ objects from a set of $N$ objects with replacement is equal to $N!$ ($N$ factorial). The number of permutations is written as ${}^{N}P$ or $P(N)$.

The number of permutations of N distinct objects taken R at a time, is given by the following expression:

$${}^{N}P_{R} = N(N-1)(N-2)(N-3)...(N-R+1)$$

$N!$

Let us take yet another example,

**Example 3.4**: How many five-letter codes in English alphabet can be written in which no letter is repeated.

**Solution**: There are 26 letters in English alphabet. The first place of the required code can be occupied by any letter from A to Z i.e., there are 26 options. Since the letters are not to be repeated, the second place can be occupied in 25 different ways, third place in 24 ways, fourth place in 23 ways and fifth place in 22 ways and so on. Therefore, the total number of possible arrangements will be $P = 26\times25\times24\times23\times22 = 7893600$

Thus, there are 7893600 unique five-letter codes that can be created by using all 26 letters of English alphabet

The example 3.4 represents a type of permutation of objects in which out of all available objects ($N$, =26) only a subset ($R$, =5) is used in the arrangement. The expression obtained in the example 3.3 can be written in terms of $N$ and $R$ as

$$P = N(N-1)(N-2)(N-3)...(N-R+1) \qquad ...(3.6)$$

This is the general expression for the possible number of permutations of $R$ objects out of a set of $N$ objects. It is represented as ${}^{N}P_{R}$ or $P(N,R)$. Multiplying and dividing by Eq. (3.6) by $(N-R)!$ we get

$${}^{N}P_{R} = N(N-1)(N-2)...(N-R+1)\times\frac{(N-R)(N-R-1).....(3)(2)(1)}{(N-R)!} \qquad ...(3.7)$$

The numerator in Eq. (3.7) becomes $N!$.Thus, the total number of permutations for choosing $R$ objects from $N$ objects without repetition is given by Eq. (3.8)

A probability distribution function is a mathematical function that expresses the distribution (variation) of the probability of the outcomes of an experiment.

$${}^{N}P_{R} = N(N-1)(N-2)(N-3)...(N-R+1) = \frac{N!}{(N-R)!} \text{for} 0<R\leq N. \qquad ...(3.8)$$

This refers to the number of permutations of $N$ objects taken $R$ at a time. You may note here that when $R = N$, the denominator becomes 0! Which is equal to 1. Therefore, the number of permutations $P(N,R) = N!$

However, if the repetition of the objects is allowed then for every object to be chosen all the $N$ objects will be available. Thus, the number of permutations for taking $R$ objects from $N$ objects with repetition, will be $N^{R}$.Similarly, the number of permutations of $N$ objects, where $R_1$objects are of one kind, $R_2$are of second kind, ..., $R_K$ are of $k^{th}$ kind is given by the expression.

$$\frac{N!}{R_1!R_2!R_3!...R_k!} \qquad ...(3.9)$$

The proof for this expression can be had from any basic book on statistics.

**Configuration**

There are certain conditions in which the order of choosing the objects is not important. For example, if you want to select two books out of three available books A, B and C, then you can select the books in the following ways:

AB, AC or BC.

In this case whether you choose A first and then B or choose B first and then A, you have the same set of books. Therefore, the order of choosing the object does not affect the outcome. You have three different combinations of two books out of three books. When the order of arranging the objects is not important, then the collection of $R$ objects out of $N$ objects is known as **combination** or **configuration**. Therefore, configuration is an unordered arrangement of $R$ objects out of $N$ objects. The key difference between a permutation and a combination is that the order of the elements in a combination does not matter, whereas it does so in case of a permutation. In simple words, there is no first place, second place, and so on, in case of combination. The combinations pqrs and prsq are identical and are not counted twice whereas these represent two of the permutations of alphabets p,q,r, and s.

Thus, the number of combinations represents all the different subsets containing $R$ items that can be sampled from $N$ distinct objects. Here, the specific arrangement of $R$ objects within a subset is irrelevant. The number of combinations can then be obtained by dividing the number of permutations $P(N,R)$ by the number of permutations of $R$ distinct objects. That is, the number of combinations equals the number of permutations of $R$ objects selected out of a total of $N$ objects divided by the number of permutations of the selected $R$ objects. Mathematically,

$$\text{Number of combinations} = {}^{N}P_{R} / R! \qquad \ldots(3.10)$$

Substituting for ${}^{N}P_{R}$ we get,

$$C(N,R) = {}^{N}C_{R} = \frac{{}^{N}P_{R}}{R!} = \frac{N!}{R!(N-R)!} \quad 0 < R \le N \qquad \ldots(3.11)$$

This can be seen as the number of combinations of $N$ objects taken $R$ at a time. You may note that $C(N,R)$ can also be visualised as the number of different arrangements of $N$ objects when $R$ of these are of one distinct type and $(N-R)$ are of a second type. Let us take up some examples to learn about the calculation of permutations and configurations for a given system.

**Example 3.5**: Calculate the number of permutations and configurations possible while selecting three balls out of five different balls taken in a box.

**Solution**: In this case, $N = 5$ and $R = 3$.

Total number of permutations

$$= {}^{5}P_{3} = \frac{5!}{(5-3)!} = \frac{5!}{2!} = \frac{5\times4\times3\times2!}{2!} = 5\times4\times3 = 60$$

Total number of combinations

$$= {}^{5}C_{3} = \frac{5!}{3!(5-3)!} = \frac{5!}{3!\times2!} = \frac{5\times4\times3!}{3!\times2\times1} = 10$$

The number of permutations is 60 whereas the configurations are just 10. This implies that for each configuration, there can be more than one permutation possible.

The expressions for number of possible outcomes for picking $R$ objects out of a total of $N$ objects under different conditions as discussed in the examples above are summarised in Table 3.1.

**Table 3.1: The expressions for number of possible outcomes for picking $R$ objects out of a total of $N$ objects under different conditions.**

| Replacement? | Ordered? | Expression |
|---|---|---|
| No | Yes | ${}^{N}P_{R} = \frac{N!}{(N-R)!}$ |
| No | No | ${}^{N}C_{R} = \frac{N!}{R!(N-R)!}$ |
| Yes | Yes | $N^{R}$ |
| Yes | No | $\frac{(N-R-1)!}{R!(N-1)!}$ |

We have so far considered situations for picking up a certain number of objects out of a given total under different conditions. Let us now take up examples of distributing objects with or without restrictions. Let us take three identical boxes and consider the distribution of a red-coloured ball amongst them. We know that it can be accomplished in three different ways, Fig. 3.1(a) i.e., the ball is in either first, second, or the third box. Now if we take two identical red balls (i.e., the balls are indistinguishable)and try to distribute them into the three identical boxes with the condition that each box can have only one ball. We find that again there are three possibilities as shown in Fig.3.1(b).

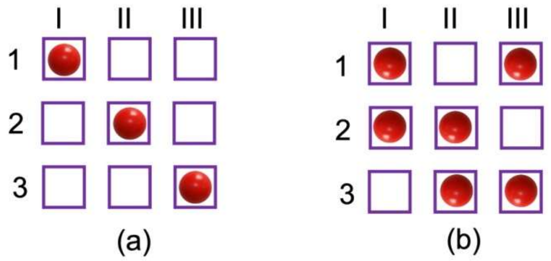


**Fig. 3.1: Possible ways of distributing (a) one and (b) two identical balls amongst three identical boxes.**

However, if we take a red and a blue ball (i.e., the balls are distinguishable now) and distribute amongst three boxes again with the condition that each box can have only one ball. We find that now there are six possible ways of doing so as shown in Fig. (3.3).

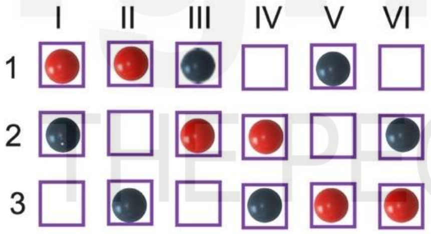


**Fig. 3.2: Possible ways of distributing two distinguishable balls amongst three identical boxes.**

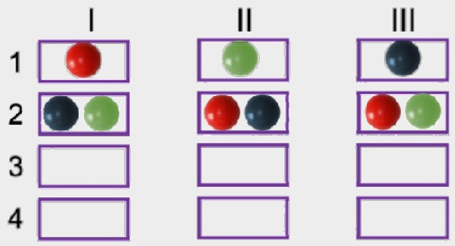
We can say that when distinguishable objects are distributed into separate subsystems there are more possible ways of doing so as compared to the indistinguishable objects. Let us take yet another example.

**Example 3.6**: a) Calculate the number of ways in which three balls of different colours can be distributed amongst four identical boxes without any restriction.

b) Calculate the number of ways if we put a condition that box 1 can have only one ball and box 2 can have two balls whereas the third and the fourth boxes have no ball at all.

**Solution**: a) Let us label the balls as R (red), B (blue) and G (green). The ball R can be placed in any of four boxes and for each of these, the ball B can also be placed in any of the four boxes. Thus, there are 4 X 4 =16 ways of placing the R and B balls. Again, for each of these there are 4 ways of placing the ball G, so the total number of ways is $4 \times 4 \times 4 = 64$.

b) Under the conditions of given restrictions, the number of ways reduces to just three. These are as shown below



In general, when a total of $N$ distinguishable objects are distributed in k boxes such that they can have $N_1, N_2, N_3, \cdots N_k$ objects respectively, then according to combinatorial mathematics the number of ways $W$ is given by the following expression.

$$W = \frac{N!}{N_1!N_2!N_3!\cdots N_k!}$$

In the present case, $N=3$, $N_1=1$, $N_2=2$, $N_3=0$ and $N_4=0$

$$W = \frac{3!}{1!2!0!0!} = 3 \text{ (Note } 0!=1)$$

Why don't you answer the following simple questions to assess your understanding?

### SAQ 4

How many 3-card arrangements can be drawn from a deck of 52 playing cards?

### SAQ 5

For an international cricket series, a group of 16 players are picked up. On the day of the match a team of 11 players is to be selected. If the captain of the team is fixed, how many 11 membered teams could be selected?

## 3.3.2 Stirling Approximation

You have learnt above that the calculation of permutation and combination (or configurations) involves the calculation of factorials. It is easier to calculate factorials for small numbers as used in the examples above. However, in chemistry we deal with very large numbers, say of the order of $10^{22}$, whose factorials are beyond the range of most computing devices. You may have noticed that common handy scientific calculator indicates 'out of range' even for 70! as the result is greater than $10^{100}$. In such cases, we can use an expression called Stirling's approximation to calculate the factorials. Let us derive the expression for the same.

The factorial of number $N$ is defined as

$$N! = N(N-1)(N-2)(N-3)...(3)(2)(1) \qquad ...(3.12)$$

Taking natural logarithm of the above expression we get,

$$\ln N! = \ln\left[N(N-1)(N-2)(N-3)\ldots(3)(2)(1)\right] \qquad \ldots (3.13)$$

$$= \ln N + \ln(N-1) + \ln(N-2) + \ln(N-3)\ldots + \ln(3) + \ln(2) + \ln(1) \qquad \ldots (3.14)$$

We can write the expression as a summation of the terms on right as

$$\ln(N!) = \sum_{N=1}^{N=N} \ln(N) \qquad \ldots (3.15)$$

Since, $N$ is very large, summation can be replaced by integration within the limits. Therefore, we can write.

$$\begin{aligned} \ln(N!) &= \int_1^N \ln N\, dN = [N\ln N - N]_1^N \\ &= \left[(N\ln N - N) - (1\ln 1 - 1)\right] \approx N\ln N - N \end{aligned} \qquad \ldots(3.16)$$

Thus, according to Stirling's approximation

$$\ln N! \sim N\ln N - N \qquad \ldots(3.17)$$

You may note that Stirling's approximation in fact approximates $\ln N!$ and not $N!$. The factorial is a product of numbers whereas $\ln N!$ is a sum which is easier to work with. The actual and approximated values of $\ln N!$ for different values of $N$ are compiled below.

| $N$ | $\ln N!$ | $N\ln N - N$ | **Percent error** |
|---|---|---|---|
| 5 | 4.79 | 3.47 | 27.56 |
| 10 | 15.10 | 13.03 | 13.71 |
| 100 | 363.74 | 360.52 | 0.89 |
| 1000 | 5912.13 | 5907.70 | 0.07 |
| 100,000 | 1051299.00 | 1051292.55 | 0.00061 |

You may note that the Stirling Approximation gives good results for very large values of $N$,however, for smaller values of $N$ the results don't match the actual value. Let us learn about the probability distribution functions. However, before that answer the following simple question to assess your understanding of Stirling approximation.

### *SAQ 6*

Calculate the percent error introduced in computing the value of 50! using Stirling approximation. (You may use a scientific calculator for the purpose).

## 3.4 PROBABILITY DISTRIBUTION FUNCTIONS

As shown above, when an experiment is carried out there are different possible outcomes, and each outcome has some probability of occurrence. To characterise a random variable, we first need the information about all the possible outcomes of the elementary events of the random variable and then get the probability of a given value as a possible outcome. Recall that in the case of tossing of a coin twice, there were four possible outcomes, and we could calculate the probability of getting a particular outcome. The **probability distribution** refers to the variation of probability of occurrence of all possible outcomes of an experiment. Each outcome has a its own probability of occurrence, however, the total probability of occurrence of all the events is always one.

Let us recall the experiment given above in which two dice are rolled simultaneously. The minimum value of the sum of the numbers on the top faces of the two dice is 1+1=2 and the maximum value of the sum is 6+6=12; the other possible sums being 3,4, 5, 6, 7, 8, 9, 10, and 11. These sums can be obtained with different permutations as shown in Table 1.2.

**Table 3.2: Number of permutations and the probabilities of different outcomes of rolling two dice.**

| Sum | Permutations | Number of permutations | Probability |
|---|---|---|---|
| 2 | 1,1 | 1 | 1/36=0.028 |
| 3 | 2,1; 1,2 | 2 | 2/36=0.056 |
| 4 | 2,2; 1,3; 3,1 | 3 | 3/36=0.083 |
| 5 | 2,3; 3,2; 1,4; 4,1 | 4 | 4/36=0.111 |
| 6 | 1,5; 2,4; 3,3; 4,2; 5,1 | 5 | 5/36=0.139 |
| 7 | 1,6; 2,5; 3,4; 4,3; 5,2; 6,1 | 6 | 6/36=0.167 |
| 8 | 2,6; 3,5; 4,4; 5,3; 6,2 | 5 | 5/36=0.139 |
| 9 | 3,6; 4,5; 5,4; 6,3 | 4 | 4/36=0.111 |
| 10 | 4,6; 5,5; 6,4 | 3 | 3/36=0.083 |
| 11 | 5,6; 6,5 | 2 | 2/36=0.056 |
| 12 | 6,6 | 1 | 1/36=0.028 |

In this case the possible outcomes for the two dice are 6 each and are independent of each other. Then, according to the fundamental counting principle, given above, the total number of possible outcomes, i.e., the number of permutations is $6^2$ =36. The last column of the table gives the probability of each possible set of permutation for the sum of the numbers on the top faces of the dice. You can clearly see that the probability depends upon the outcome. A plot (variation) of probability against the outcome is referred to as **probability distribution**.

The probability distribution is generally expressed in terms of a mathematical function of outcome i.e., the variable of interest. If $X$ is the variable of interest, then the probability distribution function is written as $P(X)$. For a specific outcome, the function is written as $P(X_i)$. In the above example, the variable of interest is the sum of the digits on the top face of the two dice with discrete values from 2 to 12. Probability of different outcomes lies between zero and one and the sum of probabilities of all the outcomes is always one.

A probability distribution function is a mathematical function that expresses the distribution (variation) of the probability of the outcomes of an experiment.

You must have realised by now that if the number of possible arrangements is small, we can easily determine them by counting. For example, in the above case the possible arrangements (permutations) or probabilities for different outcomes can be easily determined and represented by a histogram as shown in Fig. (1.4(a)).

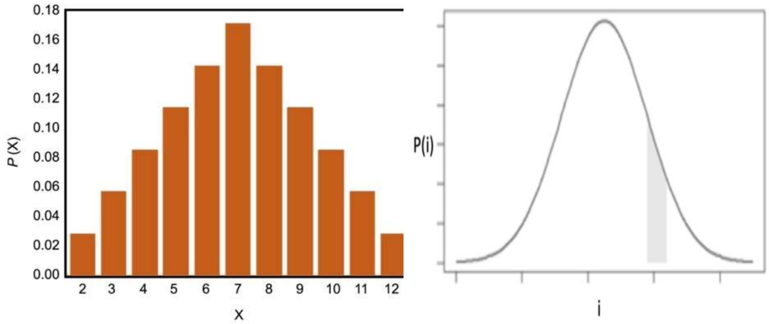


**Fig. 1.4: (a) For small number of possible outcomes the data can be represented in terms of a histogram and the total probability is the sum of the individual probabilities (b) A smooth function representing the distribution of probabilities of different outcomes; the total probability is given by the area under the curve. The shaded portion represents the possible arrangements in the selected range of outcomes.**

Since the outcomes in this experiment have discrete values the probability distribution function is called **discrete probability distribution function**. In such a case, the total number of possible arrangements can be obtained by adding the values represented by the bars in the histogram. Mathematically,

$$P(X_1)+P(X_2)+P(X_3)+\ldots=\sum_{i=1}^{N}P(X_i) \qquad \ldots(3.18)$$

The probability of a variable having the given value $f_i$ in the sample space is defined as

$$P(X_i)=\frac{f_i}{\sum_{i=1}^{N}f_i} \qquad \ldots(3.19)$$

The average value of the function is equal to the sum of the value of the function for all values of $X_i$ multiplied by the probability of the variable with the corresponding value i.e.,

$$\langle f(X)\rangle=\sum_{i=1}^{N}f(X_i)P(X_i) \qquad \ldots(3.20)$$

However, when the number of possibilities increases, it becomes increasingly difficult and time-consuming process to count the possible number of permutations. After a certain stage it becomes impossible to determine the total number of possibilities by adding the possible permutations for each outcome. In such cases where the possible outcomes do not form a discrete set but a continuum in $R$ ,the distribution of probabilities can be expressed by a smooth function (Fig. (1.4(b)) and is called **continuous probability distribution function**. The total number of possible arrangements in such cases equals the area under the curve. This can be determined by suitably integrating the probability function. In probability density function, the probability of an outcome in a small range of outcomes d$X$ is given by the expression $p(X)$d$X$. Here, $p(X)$ is called **probability density** and represents the probability of an outcome to have a value between x and x + dx. The total probability in the range is given by the following integral.

$$\int_{X_1}^{X_2} p(X)dX \qquad \ldots(3.21)$$

The probability distributions are usually normalised. It implies that these satisfy the following criteria

$$\int p(X)dX = 1 \qquad \ldots(3.22)$$

The probability of a variable having the given value $f(X)$ in the ranged $X$ is defined as

$$P(X)dX = \frac{f(X)dX}{\int_{X_1}^{X_2} f(X)dX} \qquad \ldots(3.23)$$

The probabilities can be used to determine the average values of some variable. Let us consider variable X that can have certain possible individual values $X_i$. If we represent the probability that a given value $X_i$ exists as $P_i$. Then the average value of the variable X is given as

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i \cdot P_i}{\sum_i P_i} \qquad \ldots(3.24)$$

Let us sum up what have we learnt in this unit. However, before that answer the following simple questions to assess your understanding.

*SAQ 7*

a) Calculate the number of permutations and configurations possible while selecting three toys out of four different toys labelled A, B, C, and D taken in a box.

b) Identify explicitly each combination and permuation for the three chosen toys.

## 3.5 SUMMARY

In this unit we have introduced you to an alternative approach to understand thermodynamic properties of a system by applying statistics to large collections of microscopic systems like atoms and molecules. We began the unit by discussing the relationship between classical and statistical thermodynamics. Herein we stated that whilst the classical thermodynamics ignores molecular complexity i.e., the quantum mechanical nature of the molecules, the statistical thermodynamics is based primarily on the quantum mechanical description of atoms and molecules.

Since statistical thermodynamics provides a probabilistic approach to understand the thermodynamic properties, we took up basic aspects of probability and related concepts. Herein, we introduced the concept of probability and explained the meaning of randomised variables, their types, sample space, permutations, and configurations with the help of suitable examples. Thereafter, we took up an important approximation i.e., Stirling approximation and discussed its need and importance. Then we discussed about probability distribution functions and their characteristics.

## 3.6 TERMINAL QUESTIONS

1. What is the probability of selecting a card of spade from a standard deck of 52 cards?

2. What are randomised variables? Name their types.

3. Consider that an unbiased coin is tossed thrice. List all possible outcomes and calculate the probabilities of i) getting heads exactly twice and ii) getting tails atleast once.

4. Consider that a fair dice is rolled twice and the numbers on the top face are designated as A and B. Assuming that all outcomes are equally likely

   i) Write down the sample space

   ii) Calculate the probability of the event defined as A+B=8

5. Write the expression for permutation for choosing when $R$ objects out of $N$ objects when(i) repetition is not allowed (ii) repetition is allowed (iii) where $R_1$ objects are of one kind, $R_2$ are of second kind.

6. There are a set of 20 natural amino acids. Calculate the number of tripeptides that can be created by using them under the following conditions:

   (i) The amino acids are replaced.

   (ii) The amino acids are not replaced.

## 3.7 ANSWERS

### Self-Assessment Questions

1. Thermodynamics is a phenomenological science that is based on the observations of the phenomenon in the macroscopic world. The science of thermodynamics was developed before an understanding of the nature of atoms and molecules was developed. The thermodynamics properties of a system can either be directly measured experimentally or are determined by the experimental data on other thermodynamic properties. The laws are universal.

   Statistical mechanics applies statistical tools to the quantum mechanical description of matter at microscopic i.e., atomic, and molecular level and provides a framework which predicts the macroscopic properties of the thermodynamic system.

2. The collection of all possible outcomes of an experiment is known as the sample space. In a standard deck of cards, there are three types of photo cards viz., Jack, Queen, and King. Each one of these types of photo cards can have four variants viz., hearts, spades, clubs, and diamonds. The desired outcome is the photo cards of heart of diamond. Therefore, the sample space would be:

   [Jack of heart, Queen of heart, King of heart, Jack of diamond, Queen of diamond, King of diamond.]

3. The continuous variables are the ones that can have any value in the given range of values. The sample space for the temperature of Delhi as given will be represented as

   $[\,2^{o}\text{C} \le T \le 46^{o}\text{C}]$

4. Each 3-card hand is a configuration obtained from the deck of 52-cards. Thus, the values of N and R are as follows:

   $N = 52$ and $R = 03$

   Using Eq. (3.11) we can calculate the number of possible permutations as

   $$^{N}C_{R} = \frac{N!}{R!(N-R)!}$$

   $$^{N}C_{R} = \frac{52!}{3!49!} = \frac{52 \times 51 \times 50 \times 49!}{3 \times 2 \times 1 \times 49!}$$

   Solving, we get the number of permutations as 795, 600.

5. We have a group of 16 players of which we need to pick up 11 members for the playing team. Since the choice for the captain of the team is fixed, we are left with fifteen platers from which we need to pick up 10 players.

   The number of possible teams $= \dfrac{15!}{10!5!} = \dfrac{15 \times 14 \times 13 \times 12 \times 11 \times 10!}{10! \times 5 \times 4 \times 3 \times 2 \times 1}$

   The number of possible teams = $= \dfrac{15 \times 14 \times 13 \times 12 \times 11}{5 \times 4 \times 3 \times 2 \times 1} = 3003$

6. The calculated value of 50! is = $3.0414 \text{ X } 10^{64}$

   The corresponding value of In 50! = 148.478.

   As per Stirling approximation In 50! = (50 X In 50) - 50 = 145.601

   Difference in the calculated and estimated values of In 50!

   = 148.478-145.601= 2.877

   Percentage error = (2.877 x 100)/148.478=1.94%

7. a) In this case, N= 4 and R = 3.

   Total number of permutations $= {}^{4}P_{3} = \dfrac{4!}{(4-3)!} = \dfrac{4!}{1!} = 4 \times 3 \times 2 = 24$

   Total number of combinations $= {}^{4}C_{3} = \dfrac{4!}{3!(4-3)!} = \dfrac{4!}{3! \times 1!} = \dfrac{4 \times 3!}{3! \times 1} = 4$

   b) The four combinations are ABC, ABD, ACD, and BCD. Each of these four combinations can be permuted in 3! = 6 ways. For these combinations the permutations are as under

   **ABC:** ABC, ACB, BAC, BCA, CAB, and CBA

   **ABD**: ABD, ADB, BAD, BDA, DAB, DBA

   **ACD**: ACD, ADC, CAD, CDA, DAC, DCA

   **BCD**: BCD, BDC, CDB,CBD, DBC, DCB

## Terminal Questions

1. In a standard deck of cards, there are 4 suits (hearts, spades, clubs, and diamonds) of13 cards each. Thus, the sample space consists of the 52 cards. Of these, 13 correspond to the event of interest (selecting a spade). Therefore, the required probability will be, $\frac{13}{52} = 0.25$

2. The random or **randomised variables**, or quantities are those variables whose value can change throughout the course of an experiment or series of events. There are two types of random variables viz., **discrete variables and** continuous variables.

3. In this case we have a coin that is to be tossed three times. In every toss we have two possible outcomes i.e., a head or a tail. We can write down all the possible outcomes of the experiment as follows:

| **Outcome No.** | **Toss 1** | **Toss 2** | **Toss 3** | **Outcome No.** | **Toss 1** | **Toss 2** | **Toss 3** |
|---|---|---|---|---|---|---|---|
| **1** | H | H | H | **5** | H | T | T |
| **2** | T | H | H | **6** | T | T | H |
| **3** | H | T | H | **7** | T | H | T |
| **4** | H | H | T | **8** | T | T | T |

Thus, there are a total of eight possible outcomes. The desired outcomes and the corresponding probabilities are as under

i) Getting heads exactly twice: You may note that the outcome number 2,3 and 4 i.e., three outcomes out of a total of eight meet the requirement. So the probability will be 3/8=0.375

ii) Getting tails at least once: You may note that all the outcomes except at number1 meet the requirement. So the probability will be7/8=0.875

4. The Since the dice is fair, the possible outcomes on each rolling of the dice are 1,2,3,4,5, and 6. Therefore the sample space will be

[(1,1), (1,2), (1,3), (1,4), (1,5), (1,6), (2,1), (2,2), (2,3), (2,4), (2,5), (2,6), (3,1), (3,2), (3,3), (3,4), (3,5), (3,6), (4,1), (4,2), (4,3), (4,4), (4,5), (4,6), (5,1), (5,2), (5,3), (5,4), (5,5), (5,6), (6,1), (6,2), (6,3), (6,4), (6,5), (6,6)]

The outcomes corresponding to the desired event are: (2,6), (3,5), (4,4), (5,3), (6,2)

Therefore, the probability of the event = 5/36 = 0.139

(It is important to note that the outcomes (2,6), & (6,2) are different. The outcome, (2, 6) implies that the first roll of dice gives a 2 whereas the second roll gives a 6. On the other hand (6, 2) implies that the first roll of dice gives a 6, whereas the second roll gives a 2. Similarly, (3,5), & (5,3) are also different.

5. The required expressions are as under

   (i) repetition is not allowed $^{n}P_{r} = \frac{n!}{(n-r)!}$

   (ii) repetition is allowed and $r_1$ objects are of one kind, $r_2$ are of second kind $P = \frac{n!}{r_1!r_2!}$

6. We are given a set of 20 amino acids, and we know that a tripeptide contains three amino acids. Now

   i) In the case when the amino acids are replaced, 20 amino acids are available each time to be picked up for creating the tripeptide. That is the possible number of tripeptides that can 02 be formed will be

   20 x 20 x 20 = 8000

   ii) In this case since the amino acids are not replaced, we will have a choice of 20 amino acids at the first instance but subsequently we will have respectively 19 and 18 amino acids available. That is, the possible number of tripeptides that can be formed will be

   $20 \times 19 \times 18 = 6840$

## Unit 4

# INTRODUCTION TO STATISTICAL THERMODYNAMICS-II

### Structure

4.1 Introduction

Expected Learning Outcomes

4.2 Boltzmann's Distribution

Microstates and Configurations

Derivation of Boltzmann's Distribution

4.3 Molecular Partition Functions

4.4 Canonical Ensemble

4.5 Thermodynamic Properties from Partition Function

Average energy of a molecule

4.6 Summary

4.7 Terminal Questions

4.8 Answers

## 4.1 INTRODUCTION

In the previous unit you were introduced to the basic aspects of the statistical approach to the understanding of thermodynamic properties of a system. You have learnt that statistical thermodynamics provides the link between the microscopic perspective of matter (the quantised energy levels at the atomic / molecular level) and its macroscopic or bulk (observable) properties. You have also learnt about the basic ideas of probability theory wherein you have learnt the concepts of probability and the meaning and significance of permutations and configurations and probability distribution functions.

In this unit we will continue our discussion on statistical thermodynamics and begin the unit by taking up Boltzmann distribution function. It is the cornerstone of statistical thermodynamics and tells us about the frequency of occurrence of the individual microscopic states of a system at a given temperature. In the process of deriving expression for the Boltzmann's distribution function we will introduce the crucial concept of partition function. This will be followed by formulating expressions for molecular partition functions corresponding to different types of quantised energies. We will then take up the idea of canonical ensemble and outline its significance. Towards the end of the unit, we will demonstrate how the statistical mechanics helps us determine the thermodynamic properties of the bulk matter by taking the example of calculation of average energy of a molecule.

In the next unit we will take up the fundamentals of solid state.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- define and differentiate between microstates and configurations;
- define and calculate the weight of a configuration;
- demonstrate that for extremely large number of particles, the system predominantly exists in the dominant configuration;
- derive an expression for the Boltzmann distribution function;
- outline the constraints operative while deriving Boltzmann distribution function;
- briefly describe the Lagrange's method of undetermined multipliers;
- outline the significance of Boltzmann's distribution function;
- define and explain molecular and canonical partition functions;
- derive expressions for translational, rotational, vibrational, and electronic partition functions;
- calculate electronic partition functions for a given system;
- explain the concept of canonical ensemble and outline its significance; and
- derive theexpression for average energy of a molecule using partition functions.

## 4.2 BOLTZMANN'S DISTRIBUTION

In a system containing many molecules, the available quantised energy states are occupied by different fraction of molecules. That is, the entire population of molecules is distributed among different energy states. Alternatively, we can say that the total energy of the system is distributed amongst the constituent molecules. Ludwig Boltzmann, an Austrian mathematician and physicists was the first person topropose an expression to calculate the population of different energy states. The expression is known as **Boltzmann distributionfunction**and is essentially a probability distribution function that allows to calculate the probability of finding the system in a certain energy state. It is central to the statistical approach to the thermodynamics.The Boltzmann distribution functionis a function of the energy of the state and the temperature of the system. The study was later extended by William Gibbs.

**Ludwig Eduard Boltzmann (1844-1906), Austrian physicist**

Before going into the details of Boltzmann distribution function and its significance, it is important to understand a few related terms. In the section on basic probability theory, in the previous unit,you have learnt about permutation and configuration. You are aware that each configuration is associated with one or more permutations. The probability of a configuration depends upon the number of permutations associated with it.

### 4.2.1 Microstates and Configurations

Let us now apply the concept permutation and configuration to the chemical systems. Here, instead of placing balls in boxes we would consider assigning particles (molecules or atoms) to different energy states. Let us take a simple "molecular" system consisting of three quantum particles that collectively have an energy equal to say three quanta. The energy states available for the particles have energies of $0, \varepsilon_0, 2\varepsilon_0, 3\varepsilon_0 \ldots$ and so on; where $\varepsilon_0$ represents a quantum of energy. Now, we ask a question, "What is the most probable distribution of energy?" i.e., what is the most likely way in which the total energy (3 quanta) is distributed amongst the particles of the system? To begin with, we assume that the particles are indistinguishable and try to work out possible distributions. There are three possibilities as shown below in Fig. 4.1. in the first case all the molecules are in $\varepsilon_0$ state i.e., having energy equal to 1 quantum each. In second case, the levels corresponding to energies of 0, $\varepsilon_0$ and $2\varepsilon_0$ have a molecule each whereas in the third case all the energy is with one molecule in the state of energy $3\varepsilon_0$. The other two molecules have zero energy.

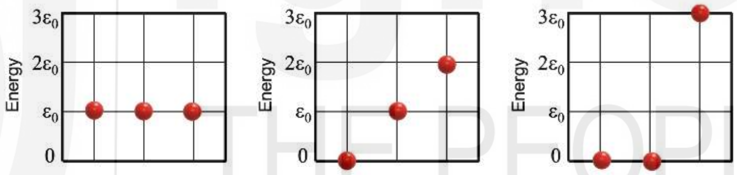


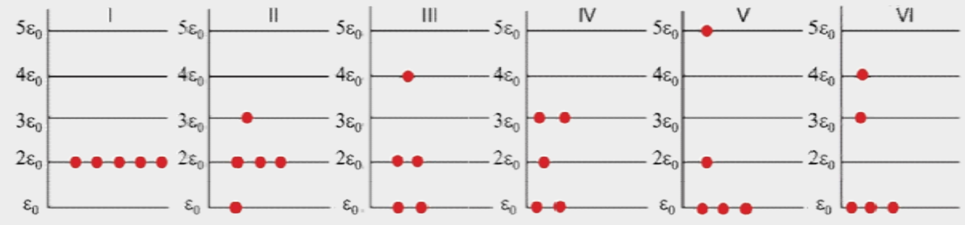
**Fig. 4.1: Three possible configurations for the distribution of three quanta of energy amongst three indistinguishable particles.**

Thus, we see in the above example, there are three different ways of arranging three particles (molecules) in various energy states such that the total energy of the system is $3\varepsilon_0$. Such arrangements of molecules in different energy states are called **configurations**. You may note that here we have assumed that the molecules are indistinguishable as indicated by their colour. Let us take one more example.

**Example 4.1**: Consider a system consisting of five indistinguishable particles ($N$ = 5) which can occupy any of the available energy levels having energies equal to $\varepsilon_0$, $2\varepsilon_0$, $3\varepsilon_0$, $4\varepsilon_0$ and $5\varepsilon_0$. If the total energy of the system is $10\varepsilon_0$, identify different possible ways in which the molecules can occupy various energy states.

**Solution**: As discussed above, in this case also there are several constraints such as the total energy of the system is fixed, the total number of molecules cannot change, and the available energy levels are also fixed. Based on these restraints, there are six different ways of arranging five particles in various energy states such that the total energy of the system is $10\varepsilon_0$ i.e., there are six configurations.

Different possible ways of distributing five indistinguishable molecules in the available energy states are shown below:


I
II
III
IV
V
VI
$5\varepsilon_0$
$4\varepsilon_0$
$3\varepsilon_0$
$2\varepsilon_0$
$\varepsilon_0$

Let us see what happens if the molecules are distinguishable. You would recall from previous unit, that when distinguishable objects are distributed into separate subsystems there are more possible ways of doing so as compared to that for the indistinguishable objects. In such cases each configuration can have one or more than one permutation possible.

The distinguishable here implies, that each particle in the system can be readily identified.

Let us reconsider the example of distribution of three quanta of energy amongst three quantum particles discussed above but now we take these particles to be distinguishable. We find that the three configurations identified for the case with indistinguishable particles can have one or more permutations as shown in Fig. 4.2. The distinguishability of the particles is indicated in terms of the colour of the spheres representing particles. The configurations 1,2 and 3 have 1,6 and 3 permutations respectively. The specific arrangement (permutations) of particles in a configuration is known as a **microstate**. In other words, we can say that *a microstate is equivalent of permutation in probability theory.*

a microstate is equivalent of permutation in probability theory.

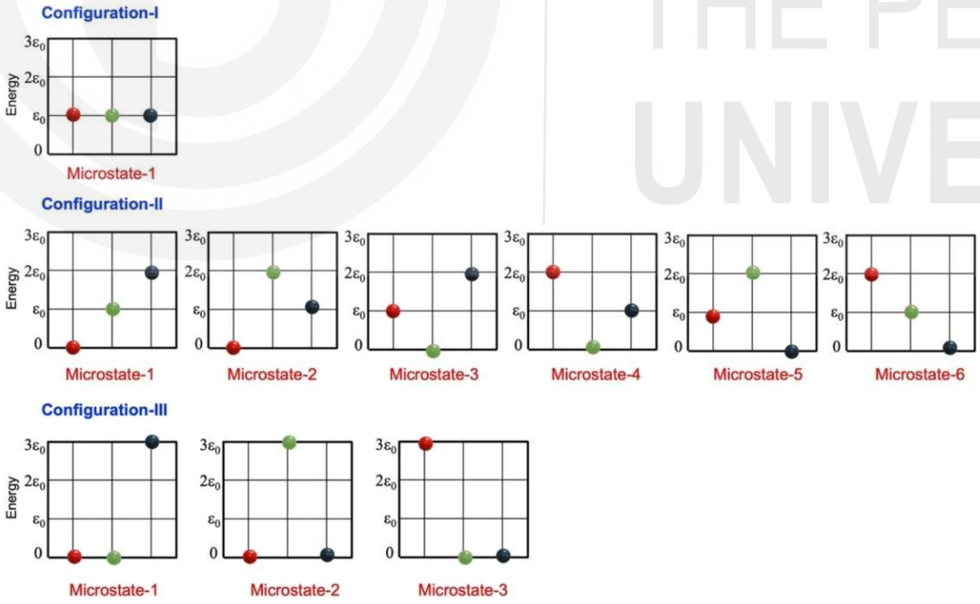

Configuration-I
Energy
$3\varepsilon_0$
$2\varepsilon_0$
$\varepsilon_0$
0
Microstate-1
Configuration-II
Microstate-1
Microstate-2
Microstate-3
Microstate-4
Microstate-5
Microstate-6
Configuration-III
Microstate-1
Microstate-2
Microstate-3

**Fig. 4.2: The configurations and the corresponding microstates for the distribution of three quanta of energy amongst three distinguishable particles.**

A configuration in this case is represented as $\{N_0, N_1, N_2, N_3\}$ where $N_0, N_1, N_2, N_3$ refer to the number of particles in the energy states $0, \varepsilon_0, 2\varepsilon_0, 3\varepsilon_0$

respectively. That is, the three configurations given above will be represented as {0,3,0,0}; {1,1,1,0}; and {2,0,0,1} respectively. It is important to note that the total energy of all the arrangements is the same and that the only difference is the distribution of the energy over the particles. The total number of microstates associated with a given configuration is known as the **weight** of the configuration and is represented by *W*. Now, a question comes up is that 'which of the possible configurations is likely to be observed for the system at equilibrium? Since all the microstates have an equal a priori probability of being observed, the probability of observing the {1,1,1,0}configuration with maximum (W=6)number of microstates, in this case, will be maximum. The probability of observing this configuration is simply the number of microstates associated with this configuration divided by the total number of microstates possible, for all the configurations put together i.e., $\frac{6}{10} = 0.6$.

The three particles case discussed above provides a general approach to determine the most probable configuration of energy for a chemical system. That is, we work out all the possible configurations of energy and determine the corresponding microstates. The configuration with the greatest number of microstates is the likely configuration. Such an approach is fine for systems with small number of particles. However, it is a daunting task to do similar exercise for any practical chemical system having astronomical number of particles. For such cases, we need to find a way to obtain the number of all the microstates associated with a configuration without any counting. Fortunately, it is possible to do work out an expression for the same. However, before that answer the following simple question to assess your understanding.

## *SAQ 1*

What is the relationship between microstates and configuration?

The problem in hand is to work out the number of possible ways of distributing $N$ distinguishable particles amongst different energy states i.e., $\varepsilon_0, \varepsilon_1, \varepsilon_2 \ldots$ such that there are $N_0, N_1, N_2, N_3 \ldots$ particles in them respectively. To begin with we assume that a given energy state can be had only by a single particle. Now, since there is a total of $N$ particles, we can assign an energy state to the first particle in $N$ different ways. Once an energy state is assigned to a particle, the next energy state can be assigned to any one of the remaining particles; and there are $(N-1)$ different ways to do so, and so on. Thus, there are $N(N-1)(N-2)\ldots 3\times 2\times 1$ i.e., $N!$ ways of assigning the energy states to $N$ distinguishable particles.

You would recall from your earlier classes that in a chemical system all the particles (atoms and molecules) do not have same energy and a given energy (or velocity) can be possessed by many particles. You may like to revisit Maxwell's distribution of molecular velocities (energies) of a gaseous sample. It implies that more than one molecule can have the same energy i.e., $N$ distinguishable particles are so assigned to different energy states, that

$N_0, N_1, N_2, N_3...$particles respectively have energies of $\varepsilon_0, \varepsilon_1, \varepsilon_2...$Thus, by considering that a given energy state can be had only by a single particle we have overestimated the possible microstates and we need to make necessary amends by correcting for the overcounting of identical permutations.

Now since each of $N_0$ particles can have energy equal to $\varepsilon_0$, there are $N_0!$ different ways in which the distinguishable particles could have been selected to have energy state, $\varepsilon_0$. Similarly, $N_1$ particles could be assigned $\varepsilon_1$ energy state in $N_1!$ and so on. Therefore, the total number of distinguishable ways of distributing $N$ particles to different energy states as required regardless of the order in which the particles were chosen i.e., the weight of a configuration is given by the following expression.

$$W = \frac{N!}{N_0!N_1!N_2!N_3!...} \qquad \text{… (4.1)}$$

In the three-particle example, $N = 3$ and we can calculate the number of microstates for different configurations as given in Table 4.1.

**Table 4.1: Number of permutations (microstates) for each configuration for a system containing 3particles with total energy equal to 3 $\varepsilon_0$.**

| Configuration | Number of particles in different energy levels | No. of Permutations (weight) | Probability |
|---|---|---|---|
| I<br>{0,3,0} | $N_0$ = 0, $N_1$ = 3, $N_2$ = 0 | $\frac{3!}{3!} = 1$ | 1/10=0.1 |
| II<br>{1,1,1} | $N_0$ = 1, $N_1$ = 1, $N_2$ = 1 | $\frac{3!}{1!1!1!} = 6$ | 6/10=0.6 |
| III<br>{2,0,1} | $N_0$ = 2, $N_1$ = 0, $N_2$ = 1 | $\frac{3!}{2!1!} = 3$ | 3/10=0.3 |
| | **Total** | **10** | **1.0** |

The probability of observing $i^{th}$ configuration is given by the weight of $i^{th}$ configuration divided by the total weight of all the configurations put together, i.e.,

$$P_i = \frac{W_i}{W_1 + W_2 + W_3 + ...W_N} = \frac{W_i}{\sum_1^N W_i} \qquad \text{… (4.2)}$$

Similarly, we can calculate the number of microstates and their probabilities for each of the configurations in Example 4.1. The results are summarised in Table 4.2. The configuration I has only one microstate, so it has the least probability (0.008) while configurations III and IV with thirty microstates each, have a probability of 0.248 each.

The possible distributions are referred to as **macrostates** or **configurations** whereas, different ways of getting the same macrostates are called **microstates** or **complexions**.

The configuration having the maximum weight is known as dominant configuration.

**Table 4.2: Number of permutations (microstates) for each configuration for a system containing 5 particles with total energy equal to 10 $\varepsilon_0$.**

| Configuration | Number of particles in different energy states | No. of Permutations (weight) | Probability |
|---|---|---|---|
| I<br>{0,5,0,0,0} | $N_2 = 5$ | $\frac{5!}{5!}=1$ | 1/121=0.008 |
| II<br>{1,3,1,0,0} | $N_1 = 1,\ N_2 = 3,\ N_3 = 1$ | $\frac{5!}{1!3!1!}=20$ | 20/121=0.165 |
| III<br>{2,1,3,0,0} | $N_1 = 2,\ N_2 = 1,\ N_3 = 2$ | $\frac{5!}{2!2!}=30$ | 30/121=0.248 |
| IV<br>{2,2,0,1,0} | $N_1 = 2,\ N_2 = 2,\ N_4 = 1$ | $\frac{5!}{2!2!}=30$ | 30/121=0.248 |
| V<br>{3,1,0,0,1} | $N_1 = 3,\ N_2 = 1,\ N_5 = 1$ | $\frac{5!}{1!3!1!}=20$ | 20/121=0.165 |
| VI<br>{3,1,0,1,0} | $N_1 = 3,\ N_3 = 1,\ N_4 = 1$ | $\frac{5!}{1!3!1!}=20$ | 20/121=0.165 |
| | **Total** | **1** | **1.0** |

You would recall from the previous unit that such a distribution is dictated by probability and the most likely distribution will correspond to a configuration with the highest number of associated permutations. Therefore, in the current example, the configurations III and IV are most likely i.e., these are dominant configurations. In other words, the configuration having the maximum weight is known as **dominant configuration**.

Let us take an example, to learn about the idea of dominant configuration.

**Example 4.2**: a) Consider a system consisting of five molecules which can occupy any of the available energy states having energies equal to0, $\varepsilon$, $2\varepsilon$, $3\varepsilon$, $4\varepsilon$ and $5\varepsilon$. If the total energy of the system is only $5\varepsilon$, calculate different possible ways in which the molecules can occupy various energy levels.

b) Repeat the exercise with

i) 50 ii) 500 and iii) 1000

molecules to be distributed amongst the same energy levels with the total energy still being $5\varepsilon$

c) Comment on the results

**Solution:** a) The possible distributions and the corresponding weights and probabilities for five molecules under given set of conditions are

| Distribution / configuration | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $N_4$ | $N_5$ | $W$ | Probability $= W/W_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 1. | 4 | 0 | 0 | 0 | 0 | 1 | 5 | 0.04 |
| 2. | 3 | 1 | 0 | 0 | 1 | 0 | 20 | 0.16 |
| 3. | 3 | 0 | 1 | 1 | 0 | 0 | 20 | 0.16 |
| 4. | 2 | 2 | 0 | 1 | 0 | 0 | 30 | **0.24** |
| 5. | 2 | 1 | 2 | 0 | 0 | 0 | 30 | **0.24** |
| 6. | 1 | 3 | 1 | 0 | 0 | 0 | 20 | 0.16 |
| | | | | | | **Total** | **125** | **1.00** |

Here, the configuration number 4 and 5 are the dominant configurations with a probability of 0.24 each.

b) i) The possible distributions and the corresponding weights and probabilities for fifty molecules under same set of conditions (total energy = $5\varepsilon$) are

| Distribution | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $N_4$ | $N_5$ | $W$ | Probability $= W/W_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 1. | 49 | 0 | 0 | 0 | 0 | 1 | 50 | 0.00 |
| 2. | 48 | 1 | 0 | 0 | 1 | 0 | 2450 | 0.00 |
| 3. | 48 | 0 | 1 | 1 | 0 | 0 | 2450 | 0.00 |
| 4. | 47 | 2 | 0 | 1 | 0 | 0 | 58800 | 0.02 |
| 5. | 47 | 1 | 2 | 0 | 0 | 0 | 58800 | 0.02 |
| 6. | 46 | 3 | 1 | 0 | 0 | 0 | 921200 | 0.29 |
| 7. | 45 | 5 | 0 | 0 | 0 | 0 | 2118760 | **0.67** |
| | | | | | | **Total** | **3162510** | **1.00** |

Here, the configuration number 7 is the dominant configuration, with the probability of 0.67.

ii) The possible distributions and the corresponding weights and probabilities for five hundred molecules under conditions of total energy = $5\varepsilon$ are

| Distribution | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $N_4$ | $N_5$ | $W$ | Probability $= W/W_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 1. | 499 | 0 | 0 | 0 | 0 | 1 | 500 | $1.182 \times 10^{-9}$ |
| 2. | 498 | 1 | 0 | 0 | 1 | 0 | 249500 | $9.392 \times 10^{-7}$ |
| 3. | 498 | 0 | 1 | 1 | 0 | 0 | 249500 | $9.392 \times 10^{-7}$ |
| 4. | 497 | 2 | 0 | 1 | 0 | 0 | 62125500 | 0.00023 |
| 5. | 497 | 1 | 2 | 0 | 0 | 0 | 62125500 | 0.00023 |
| 6. | 496 | 3 | 1 | 0 | 0 | 0 | 10292124500 | 0.0387 |
| 7. | 495 | 5 | 0 | 0 | 0 | 0 | 255244687600 | **0.9608** |
| | | | | | | **Total** | **265661562600** | **1.00** |

As the number of molecules increases, the weight of the most probable configuration/ probability of the dominant configuration also increases.

Here again, the configuration number 7 is the dominant configuration, but with a probability of 0.96; it has increased substantially.

ii) The possible distributions and the corresponding weights and probabilities for one thousand molecules under conditions of total energy = $5\varepsilon$ are

| **Distribution** | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $N_4$ | $N_5$ | $W$ | $W/W_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 1. | 999 | 0 | 0 | 0 | 0 | 1 | 1000 | $1.188 \times 10^{-10}$ |
| 2. | 998 | 1 | 0 | 0 | 1 | 0 | 999000 | $1.868 \times 10^{-7}$ |
| 3. | 998 | 0 | 1 | 1 | 0 | 0 | 999000 | $1.868 \times 10^{-7}$ |
| 4. | 997 | 2 | 0 | 1 | 0 | 0 | 498001500 | $5.916 \times 10^{-5}$ |
| 5. | 997 | 1 | 2 | 0 | 0 | 0 | 498001500 | $5.916 \times 10^{-5}$ |
| 6. | 996 | 3 | 1 | 0 | 0 | 0 | 165668499000 | 0.01968 |
| 7. | 995 | 5 | 0 | 0 | 0 | 0 | 8250291250200 | **0.9802** |
| | | | | | | **Total** | **8416957751200** | **1.00** |

Here also the configuration number 7 is the dominant configuration. Now, it has a calculated probability of 0.98.

c) On the basis of the calculations given above, we note that as the number of molecules increases, the weight of the most probable configuration/ probability of the dominant configuration also increases.

From the above example, we conclude that as the size of the system increases, the weight / probability of the dominant configuration goes on increasing and at a certain stage the dominant configuration outweighs the rest of the configurations. That is, the probability of dominant configuration is so high that the system predominantly exists in the dominant configuration. All microstates have equally a priori probabilities i.e., these are equally probable. However, large number of them being associated with the most probable macrostates makes them much more probable than other possible microstates. In such cases $W$ becomes the number of microstates for a given macrostates or configuration. The energy distribution in the dominant configuration is referred to as the **most probable energy distribution**.

In real systems we deal with astronomically high number ($N \sim 10^{22\text{-}23}$)of particles. The available numbers of energy levels are also very large. From the above examples we can say that in real systems, $W$ for the most probable distribution is so close to $W_{tot}$ that its probability is ~1. Thus, for real systems we need to find $W_{tot}$ which is almost same as $W$ for the most probable distribution.In other words, we need to find the distribution of energy amongst the particles in the most probable state.

You may recall that we raised a question above, that '*what is the most probable distribution of the particles in a system at thermal equilibrium*?' We are now equipped to take up this question for a chemical system. We can visualise such a system at equilibrium in terms of many particles that are so arranged that they can exchange energy with one another. The particles in a group have a certain average energy, but at any instant, the energy content of each particle fluctuates around the average value due to the energy exchange with other particles. Also, we need to note that the particles are independent of each other, implying that at given instant the energy of a given particle is independent of the energy of all the other particles. Thus, the energies of the particles are distributed according to a specific probability distribution function that depends on the equilibrium temperature. Boltzmann's distribution function is such a distribution function.

So, the issue boils down to determining the most probable distribution without having to find any of the less probable distributions. As stated above, the dominant configuration has the largest weight. If the system changes to any other configuration, it's weight will decrease. Thus, we can say that the dominant configuration corresponds to the peak or maxima of the plot of the weight as a function of some identifier of the configurations. Let us derive an expression for Boltzmann's distribution.

However, before that answer the following simple questions to assess your understanding.

*SAQ 2*

Determine the possible ways of distributing 7 distinguishable particles among 4 energy levels with energies of 0, 1,2, and 3 quanta such that the total energy is equal to 3 quanta.

*SAQ 3*

Repeat the calculation in Example 4.2 for 100 molecules under same conditions and calculate the $W/W_{\mathrm{Tot}}$ ratio for the dominant configuration.

## 4.2.2 Derivation of Boltzmann Distribution

We have shown above (Eq. 4.1) that the weight of a configuration depends on the values of all the $N_i$'s in it. So, to determine the dominating configuration we need to find the value of $N_i$ that maximises the function $W$. This can be achieved by varying the values of $N_i$ and looking for the values that correspond to $\mathrm{d}W = 0$. You would recall from your earlier classes that to determine the maxima for a function we have to equate its first derivative to zero. However, in case of systems with many particles it is mathematically convenient to maximise the function $\ln W$ instead. It is so because firstly for large value of $N$, the value of $W$ will be very large and secondly, for $\ln W$ we can employ Stirling's approximation discussed above. Let us take natural logarithm of Eq. (4.1), and simplify, we get.

$$\ln W = \frac{\ln N!}{\ln(N_0!N_1!N_2!N_3!\ldots)} \quad \ldots (4.3)$$

$$\ln W = \ln N! - \ln(N_0!N_1!N_2!N_3!\ldots) \quad \ldots (4.4)$$

$$\ln W = \ln N! - \ln N_0! - \ln N_1! - \ln N_2!\ldots \quad \ldots (4.5)$$

Putting the $\ln N_i$ together, we can write.

$$\ln W = \ln N! - \sum_i \ln N_i! \qquad \ldots (4.6)$$

Using Stirling's approximation, the above equation is written as

$$\ln W = (N \ln N - N) - \sum_i \{N_i \ln N_i - N_i\} \qquad \ldots (4.7)$$

Since, $\sum_i N_i = N,$ we can write,

$$\ln W = N \ln N - N + N - \sum_i N_i \ln N_i = N \ln N - \sum_i N_i \ln N_i \qquad \ldots (4.8)$$

Let us note that a change in the configuration of a system is accompanied by the change in the population of each state $i$ from $N_i$ to $N_i + dN_i$ The corresponding change in $\ln W$ can be given as

$$d \ln W = \sum_i \left( \frac{\partial \ln W}{\partial N_i} \right) dN_i = 0 \qquad \ldots (4.9)$$

The term on right hand side gives the summation of the rate of change of $\ln W$ with $N_i$ multiplied by the total change in $N_i (dN_i)$. For $\ln W$ to be maximum, this sum must be equal to zero.

So far, we have considered all the states to have same energy, implying that all the configurations have the same total energy. Let us extend the argument now to different states having different energies i.e., $\varepsilon_0, \varepsilon_1, \varepsilon_2 \ldots$ Since an isolated system has a constant total energy so we can retain only those configurations that have this total energy i.e., the configurations must satisfy the following condition.

$$\sum_i N_i \varepsilon_i = E \qquad \ldots (4.10)$$

In other words, one particle in the collection is free to gain or lose energy, but a corresponding amount of energy must decrease elsewhere in the system. Thus, the following condition should hold.

$$\sum_i \varepsilon_i dN_i = 0 \qquad \ldots (4.11)$$

The Eq. (4.10) and Eq. (4.11) represent the energy constraint on the system. Now, since the total number ($N$)of particles in the system are fixed, we cannot vary the populations of all the energy states independently. A change in the population of any state must be accompanied by the corresponding changes in the population of other state (s), i.e., the decrease in the population of a state number must be balanced by an increase in the population of another state. Mathematically

$$\sum_i N_i = N \qquad \ldots (4.12)$$

It demands that the sum of all the changes in $dN_i$ must be zero. That is

$$\sum_i dN_i = 0 \qquad \ldots (4.13)$$

The Eq. (4.12) and Eq. (4.13) represent the number constraint of the system. Thus, the problem reduces to solving the Eq. (4.9) under the constraints as given in Eqs. (4.11) and (4.13). For this we will use Lagrange's method of undetermined multipliers discussed later. This method allows to determine the maximum value of a function that depends on many variables. In this method each constraint is multiplied by a coefficient and the resultant is added to the main equation. The variables are assumed to vary independent of each other and the values of coefficients are then determined. However, before using this method we simplify the expression to be maximised.

For this we rewrite Eq. (4.8) by labelling the states by $j$ in place of $i$ as

$$\ln W = N \ln N - \sum_j N_j \ln N_j \qquad \ldots (4.14)$$

Differentiating the equation w. r. t., $N_i$, we get

$$\frac{d \ln W}{dN_i} = \frac{dN \ln N}{dN_i} - \sum_j \frac{N_j \ln N_j}{dN_i} \qquad \ldots (4.15)$$

Solving the terms of right-hand side using differentiation by parts, we get

$$\frac{d \ln W}{dN_i} = \frac{dN}{dN_i} \ln N + N \frac{d \ln N}{dN_i} - \sum_j \left[ \left(\frac{dN_j}{dN_i}\right) \ln N_j + N_j \left(\frac{d \ln N_j}{dN_i}\right) \right] \qquad \ldots (4.16)$$

We know that

$$N = N_0 + N_1 + N_2 + \ldots + N_i + \ldots \qquad \ldots (4.17)$$

Since $N_j$ is independent of $N_i$, when we differentiate Eq. (4.17) w. r. t., $N_i$, the derivative for the $i^{th}$ term on the right will be unity whereas for all the other terms ( $j$ terms) it will vanish. That is $\frac{dN_j}{dN_i} = 1$ when $i = j$.and ,$\frac{dN_j}{dN_i} = 0$ when $i \neq 0$ This fact can be represented in terms of a delta function as

$$\frac{dN_j}{dN_i} = \delta_{ij} \qquad \ldots (4.18)$$

where $\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$. Thus, we can write.

$$\frac{dN}{dN_i} = 1 \qquad \ldots (4.19)$$

Also, we can write.

$$\frac{d \ln N}{dN_i} = \frac{1}{N} \qquad \ldots (4.20)$$

and $$\frac{d \ln N_j}{dN_i} = \frac{1}{N_j} \frac{dN_j}{dN_i} \qquad \ldots (4.21)$$

Using Eq. (4.18) to Eq. (4.21)we can write Eq. (4.16) as

$$\frac{d \ln W}{dN_i} = [(1 \times \ln N) + (N \times \frac{1}{N})] - \sum_j \left[ (0 \times \ln N_j) + N_j \times \frac{1}{N_j} \frac{dN_j}{dN_i} \right] \qquad \ldots (4.22)$$

$$\frac{d\ln W}{dN_i} = (\ln N + 1) - \sum_j \left[\frac{dN_j}{dN_i}\ln N_j + \frac{dN_j}{dN_i}\right] \qquad \dots (4.23)$$

$$\frac{d\ln W}{dN_i} = (\ln N + 1) - \sum_j \delta ij(\ln N_j + 1) \qquad \dots (4.24)$$

Simplifying we get

$$\frac{d\ln W}{dN_i} = (\ln N + 1) - (\ln N_i + 1) \qquad \dots (4.25)$$

$$\frac{d\ln W}{dN_i} = \ln N - \ln N_i = -\ln\frac{N_i}{N} \qquad \dots (4.26)$$

Since for the dominant configuration, $\frac{d\ln W}{dN_i} = 0$, for all values of $N_i$ we write.

$$d\ln W = \sum_i -\ln\frac{N_i}{N}dN_i = 0 \qquad \dots (4.27)$$

This is the simplified version of Eq. (4.9). Let us come back to *Lagrange's method of undetermined multipliers and apply it to the simplified expression,*Eq. (4.27). We multiply the Eq. (4.11) by an unknown coefficient α and Eq. (4.13) by an unknown coefficient, −β and add these terms to Eq. (4.27),we get

$$d\ln W = \sum_i -\ln\frac{N_i}{N}dN_i + \alpha\sum_i dN_i - \beta\sum_i \varepsilon_i dN_i = 0 \qquad \dots (4.28)$$

Using Eq. (4.26) we can write the right-hand side of the Eq. (4.28) as

$$\sum_i \left(\frac{d\ln W}{d\,N_i}\right)dN_i + \alpha\sum_i dN_i - \beta\sum_i \varepsilon_i dN_i = 0 \qquad \dots (4.29)$$

Rearranging the terms, we get

$$\sum_i \left\{-\ln\frac{N_i}{N} + \alpha - \beta\varepsilon_i\right\}dN_i = 0 \qquad \dots (4.30)$$

Since we have started the derivation by making a small change in $N_i$ so d$N_i$ is not zero. Therefore, Eq. (4.30) will be valid when the term in the brackets is equal to zero, i.e.,

$$-\ln\frac{N_i}{N} + \alpha - \beta\varepsilon_i = 0 \qquad \dots (4.31)$$

or $$\left(\frac{d\ln W}{dN_i}\right) + \alpha - \beta\varepsilon_i = 0 \qquad \dots (4.32)$$

Rearranging Eq. (4.31) we get

$$\ln\frac{N_i}{N} = -(-\alpha + \beta\varepsilon_i) = \alpha - \beta\varepsilon_i \qquad \dots (4.33)$$

Taking the antilogarithm, we get

$$\frac{N_i}{N} = e^{\alpha}.e^{-\beta\varepsilon_i} \qquad \dots (4.34)$$

$$\Rightarrow N_i = Ne^{\alpha}.e^{-\beta\varepsilon_i} \qquad \dots (4.35)$$

This equation is the mathematical form of Boltzmann distribution. It gives the number of molecules in the $i^{th}$ energy state of the dominant configuration.

$\frac{N_i}{N}$ is also equal to the probability of occupation of the given energy level. To appreciate the significance of Eq. (4.35) we need to determine the unknown multipliers i.e., the coefficient α and β.

**Determination of α**

We know that the sum of the populations $N_i$ of the states is equal to the total number of molecules, $N$ i.e.,

$$\sum_i N_i = N \qquad \dots (4.12)$$

Using Eq. (4.35) and substituting for $N_i$, we can write,

$$\sum_i Ne^{\alpha}.e^{-\beta\varepsilon_i} = N \qquad \dots (4.36)$$

Simplifying and cancelling N on both sides we get

$$Ne^{\alpha}\sum_i e^{-\beta e\varepsilon_i} = N \qquad \dots (4.37)$$

$$e^{\alpha}\sum_i e^{-\beta\varepsilon_i} = 1 \Rightarrow\Rightarrow e^{\alpha} = \frac{1}{\sum_i e^{-\beta\varepsilon_i}} \qquad \dots (4.38)$$

The term in the denominator is called partition function and is represented as $q$ i.e.,

$$\text{Partition function} = q = \sum_i e^{-\beta\varepsilon_i} \qquad \dots (4.39)$$

Pending the determination of coefficient$\beta$, we can visualise the partition function to describe the distribution of energy in a system. For example, using the partition function with Eq. (4.35), we find that the probability Pi of occupying a given energy level $i$ becomes

$$p_i = \frac{N_i}{N} = e^{\alpha}.e^{-\beta\varepsilon_i} = \frac{e^{-\beta\varepsilon_i}}{q} \text{ or } \frac{N_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} \qquad \dots (4.40)$$

Eq.(4.40) is the an important result. It quantifies the probability of occupying a given energy for the dominant configuration of energy. This well-known and important result is referred to as the **Boltzmann distribution**. Comparing Eq.(4.40) to the expression for probability involving discrete variables, viz.,

$$P(X_i) = \frac{f_i}{\sum_{j=1}^{M} f_j} \qquad \dots (4.41)$$

we find that the Boltzmann distribution is nothing more than a statement of probability, with the partition function serving to normalize the probability distribution.

### Determination of β

In Eq. (4.40), since the exponent ($\beta\varepsilon_i$) should be unitless, the coefficient $\beta$ must have unit of inverse of energy. This implies that $\beta$ must be related to energy. We can derive $\beta$ by studying the variation of weight of the dominant configuration with energy. Let us recall Eq. (4.14),

$$\ln W = N\ln N - \sum_j N_j \ln N_j \qquad \text{… (4.14)}$$

The differential form of the equation can be written as

$$d\ln W = d(N\ln N) - \sum_j d(N_j \ln N_j) \qquad \text{… (4.42)}$$

Since $N$ is the total population of the system and does not change, the first term of Eq. (4.42) will be zero (i.e., d($N$ ln $N$) = 0. Solving the second term on the right side of the equation we can write,

$$d\ln W = -\sum_j \left\{ \ln N_j dN_j + N_j d\ln N_j \right\} \qquad \text{… (4.43)}$$

Simplifying using Eq. (4.21), we get

$$d\ln W = -\sum_j \left\{ \ln N_j dN_j + dN_j \right\} = -\sum_j \ln N_j dN_j - \sum_j dN_j \qquad \text{… (4.44)}$$

Since, $\sum_j dN_j = 0$, we get $d\ln W = -\sum_j \ln N_j dN_j$ … (4.45)

From Eq. (4.35) we have

$$N_j = Ne^{\alpha}.e^{-\beta\varepsilon_j} \qquad \text{… (4.35)}$$

For the lowest energy state with energy $\varepsilon_0$, the population is given by the expression.

$$N_0 = Ne^{\alpha}.e^{-\beta\varepsilon_0} \qquad \text{… (4.46)}$$

Therefore, the population of any state with respect to the ground state is

$$\frac{N_j}{N_0} = \frac{e^{-\beta\varepsilon_j}}{e^{-\beta\varepsilon 0}} = e^{-\beta(\varepsilon_j \varepsilon_0)} \qquad \text{… (4.47)}$$

By convention, the ground state energy is taken as zero and rest of the energy states are scaled from it. Therefore,

$$N_j = N_0 e^{-\beta\varepsilon_j} \qquad \text{… (4.48)}$$

Taking logs,

$$\ln N_j = \ln N_0 - \beta\varepsilon_j \qquad \text{… (4.49)}$$

Substituting the above expression in Eq. (4.45) we get

$$d\ \ln W = \sum_j (\ln N_0 - \beta\varepsilon_j) dN_j \qquad \text{… (4.50)}$$

$$d\ln W = -\ln N_0 \sum_j dN_j + \beta \sum_j \varepsilon_j dN_j \qquad \text{… (4.51)}$$

Since $\sum_j dN_j = 0$ and $\sum_j \varepsilon_j dN_j = dE$ … (4.52)

We write, $d\ln W = \beta dE$ … (4.53)

You can note that $\beta$ has the unit of inverse of energy. Let us now consider two systems, 1 and 2 having distinguishable particles with the weight of dominant configurations as $W_1$and $W_2$respectively. Let us assume that these are brought together to form an isolated composite system. At the time of mixing, the weight of the composite configuration will be $W_1.W_2$. The system will then attain equilibrium with some change in the configuration. Let the change in configuration = d($W_1.W_2$).

Since equilibrium results in a configuration with greater weight,

$$d(W_1.W_2) \geq 0 \text{or} W_2dW_1 + W_1dW_2 \geq 0 \quad \text{… (4.54)}$$

Dividing the Eq. (4.54) by $W_1.W_2$ we get

$$\frac{dW_1}{W_1} + \frac{dW_2}{W_2} \geq 0 \quad \text{… (4.55)}$$

Writing in the derivative form

$$d\ln W_1 + d\ln W_2 \geq 0 \quad \text{… (4.56)}$$

Substituting from Eq. (4.53)

$$\beta_1 dE_1 + \beta_2 dE_2 \geq 0 \quad \text{… (4.57)}$$

Here, $\beta_1$and $\beta_2$ are values of $\beta$ for systems before mixing. $dE_1$ and $dE_2$ are the changes in the energies of the two system on mixing. Since the composite system is isolated

$$dE_1 + dE_2 = 0 \quad \text{… (4.58)}$$

Let$dE_1 > 0$, then $dE_2 < 0$. This implies that the initially $E_2$ was greater than $E_1$. Therefore, since temperature is a measure of energy, $T_2 > T_1$.In this case, for Eq. (4.57) to be valid, $\beta_1 \geq \beta_2$. Since $\beta$ is inversely related to energy, it must also be inversely related to temperature.

$$\beta \propto \frac{1}{T} \quad \text{… (4.59)}$$

Removing the proportionality sign, we get

$$\beta = \frac{1}{kT} \quad \text{… (4.60)}$$

Here, $k$ is known as Boltzmann constant and has a value of $1.38 \times 10^{-23}\,\text{JK}^{-1}$

The Boltzmann distribution, Eq. (4.40) can be written as

$$\frac{N_i}{N} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{q} \text{ or } N_i = \frac{N}{q} e^{-\varepsilon_i/kT} \quad \text{… (4.61)}$$

The denominator of Eq. (4.61) is termed **particle partition function** or **molecular partition function** and is represented as $q$. It is one of the most important quantities in statistical thermodynamics and will be taken up in details in the next section. We can write the Eq. (4.61) by using the expression for partition function from Eq. (4.39) as

$$N_i = N\frac{e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}} \qquad \dots (4.62)$$

According to the Boltzmann distribution law if the energy associated with some energy state of a system is ε then the probability of its occurrence, is proportional to $e^{-\frac{\varepsilon}{kT}}$

This is the mathematical expression for the Boltzmann distribution law and signifies that if the energy associated with some state or condition of a system is ε then the frequency with which that state or condition occurs, or the probability of its occurrence, is proportional to

$$e^{-\frac{\varepsilon}{kT}} \qquad \dots (4.63)$$

where $T$ is the system's absolute temperature and k is the Boltzmann constant. You may note here that at a given temperature, since the energies of all the levels are positive, $k$ is also a positive constant and $T$ is always positive, the population of the levels decreases exponentially with an increase in the energy of the level. In other words, the ground state has the largest population, and the population of excited states goes on decreasing; higher the energy, lower the population. Let us take an example to understand its application.

**Example 4.3:** A molecule can be in any of the two states. It's excited state is separated from its ground state by $8.0\times10^{-21}$ J. If the ground state has energy = 0, calculate the fraction of molecules in the excited state at 300 K.

**Solution**: we know that according to Boltzmann's law

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}$$

Now let us first calculate the denominator by substituting the exponents.

$$\sum_i e^{-\varepsilon_i/kT} = e^0 + e^{-\varepsilon_1/kT} = 1 + e^{-\frac{8.0\times10^{-21}\,\mathrm{J}}{(1.381\times10^{-23}\,\mathrm{JK^{-1}})(300K)}}$$

Solving, we get

$$\sum_i e^{-\varepsilon_i/kT} = 1 + e^{-\frac{8.0\times10^{-21}\,\mathrm{J}}{(1.381\times10^{-23}\,\mathrm{JK^{-1}})(300K)}} = 1 + e^{-1.931} = 1.145$$

The the fraction of molecules in the excited state can then be calculated as

$$\frac{N_i}{N} = \frac{e^{-\frac{8.0\times10^{-21}\,\mathrm{J}}{(1.381\times10^{-23}\,\mathrm{JK^{-1}})(300K)}}}{1.145} = \frac{0.145}{1.145} = 0.127$$

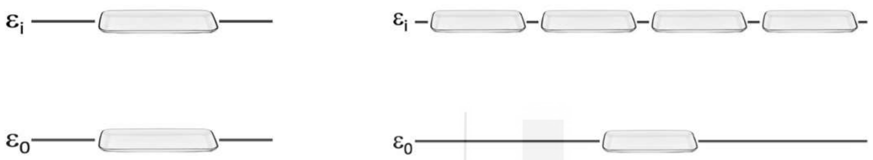
Thus, fraction of molecules in the excited state at 300 K would be = 0.127 i.e., about 12.7% of the molecules will be in excited state.

The Eq. (4.62) gives the population of $i^{th}$ level w.r.t., the ground state. The ratio of population of two different energy levels ($i^{th}$ and $j^{th}$) can be determined by eliminating the partition function between them as follows.

$$\frac{N_i}{N_j} = \frac{e^{-\frac{\varepsilon_i}{kT}} / q}{e^{-\frac{\varepsilon_j}{kT}} / q} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{e^{-\frac{\varepsilon_j}{kT}}} = e^{-\frac{(\varepsilon_i - \varepsilon_j)}{kT}} \qquad \dots (4.64)$$

## Degeneracy and Boltzmann Distribution

So far, we have considered a case where each energy level is associated with one energy state. You would have learnt in earlier classes that the quantised energy levels are composed of a finite number of allowed *energy states.*



**(a)** **(b)**

**Fig. 4.1: Schematic representation of energy levels and their degeneracies. (a) both the levels are singly degenerate (b) The $\varepsilon_0$ level is singly degenerate whereas level $\varepsilon_1$ has a degeneracy of 4.**

The energy states having same energy are said to be **degenerate**. The number of such energy states for $i^{th}$ energy level is termed as its ***degeneracy*** and is denoted as $g_i$. We can visualise such an energy level, as a shelf with a known number of boxes/ trays equal to the value of the degeneracy, $g_i$ as shown in Fig. 4.1(b). The height of each shelf represents the energy of the level, and the trays indicate the possible locations for the molecules in the energy level. Now the question is, how does degeneracy influence probability? Let us consider two systems the first with single states at energy $\varepsilon_0$ and $\varepsilon_i$ as shown in Fig. 4.1(a) and the second system in which four states are present at energy level, $\varepsilon_i$, Fig. 4.1(b). To simplify the calculations, we write the expression for the partition function as

$$q_{system1} = \sum_i g_i e^{-E_i} \quad where \quad E_i = \varepsilon_i / kT \qquad \dots (4.65)$$

The partition function for the first system will be

$$q_{system1} = \sum_i g_i e^{-E_i} = 1e^0 + 1e^{-1} = 1 + 0.37 = 1.37$$

Whereas for the second system

$$q_{system1} = \sum_i g_i e^{-E_i} = 1e^0 + 4e^{-1} = 1 + 1.48 = 2.48$$

It is important to note that all the degenerate energy states will have equal probability of occupation. That is, the total probability of occupation of a given energy level with degeneracy $g_i$ is equal to

$$p_i = \frac{g_i e^{-\varepsilon_i / kT}}{q} \qquad \dots (4.66)$$

The probabilities of energy level $\varepsilon_i$ being occupied in the two cases would be.

$$p_{system1} = \frac{0.37}{1.37} = 0.27$$

$$p_{system2} = \frac{1.48}{2.48} = 0.60$$

It is important to note that depending on their nature, some microscopic particles can be occupied in a way that there is single particle per energy state whereas some other particles, do not have such a limit on their occupancy. Thus, the particles could either be distinguishable or indistinguishable and may singly occupy an energy state or any number of these can be present in an energy state. Let us now take up a very important concept i.e., partition function. However, before that answer the following simple questions to assess your understanding.

## *SAQ 4*

A molecule can be in any of the two states. Its excited state is separated from its ground state by 1.60 x $10^{-22}$ J. If the ground state has energy = 0, calculate the fraction of molecules in the excited state at

i) 300 K ii) 1000 K

Compare the results with the one obtained in Example 4.3.

## 4.3 MOLECULAR PARTITION FUNCTIONS

In the beginning of the unit, we stated that statistical thermodynamics acts as a bridge between molecular (microscopic) properties and the bulk properties of the macroscopic system. The partition function is the tool that relates the properties of molecule to the macroscopic properties of the system. As discussed above, the partition function is mathematically defined as

$$q = \sum_i e^{-\varepsilon_i/kT} \qquad \text{… (4.67)}$$

This gives the sum over all the energy states in Boltzmann distribution. Recall that Boltzmann distribution gives the distribution of molecules over different energy levels in the dominant configuration. Therefore, the partition function is also known as **molecular partition function**. While considering Boltzmann distribution, we had assumed that the degeneracy of all the energy levels is one. However, since molecules have many degenerate energy levels, it is important to include degeneracy in the expression for partition function. Therefore, the molecular partition function can also be written as

$$q = \sum_i g_i e^{-\varepsilon_i/kT} \qquad \text{… (4.68)}$$

Here, $g_i$ is the degeneracy of the $i^{th}$ energy level.

Until now we have discussed the total energy of a molecule for a given energy state. You know that the total energy of the molecule has contribution from translational energy, rotational energy, vibrational energy, and electronic energy of the molecule i.e.,

$$\varepsilon_{i,total} = \varepsilon_{i,trans} + \varepsilon_{i,rot} + \varepsilon_{i,vib} + \varepsilon_{i,el} \quad \dots (4.69)$$

Further, you would recall that according to Born-Oppenheimer approximation these energies can be taken as independent of each other. Thus, the molecular partition function without considering degeneracy can be written as

$$q = \sum_i e^{-\frac{(\varepsilon_{i,trans}+\varepsilon_{i,rot}+\varepsilon_{i,vib}+\varepsilon_{i,el})}{kT}} \quad \dots \quad (4.70)$$

$$q = \sum_i e^{-\frac{(\varepsilon_{i,trans})}{kT}} \cdot e^{-\frac{(\varepsilon_{i,rot})}{kT}} \cdot e^{-\frac{(\varepsilon_{i,vib})}{kT}} \cdot e^{-\frac{(\varepsilon_{i,el})}{kT}} \quad \dots (4.71)$$

Separating each term and introducing degeneracy for each type of energy level we get

$$q = \sum_i g_{i,trans} e^{-\frac{(\varepsilon_{i,trans})}{kT}} \cdot \sum_i g_{i,rot} e^{-\frac{(\varepsilon_{i,rot})}{kT}} \cdot \sum_i g_{i,vib} e^{-\frac{(\varepsilon_{i,vib})}{kT}} \cdot \sum_i g_{i,el} e^{-\frac{(\varepsilon_{i,el})}{kT}} \quad \dots (4.72)$$

$$q = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdot q_{el} \quad \dots (4.73)$$

Thus, the total partition function is the product of partition functions of each type of the energies of the molecule. This is known as **factorization of partition function**. We can calculate the contribution of each type of partition function to the total partition function separately and put them together to get the total partition function. Let us learn how do we calculate the partition function of each type of energy. For this, we need to know their respective expressions for quantised energy. Here, we will be using the expression without deriving them. You must have learnt about their derivation during your earlier studies on quantum mechanics. We will take up the following four types of partition functions.

I. Translational partition functions
II. Rotational partition functions
III. Vibrational partition function
IV. Electronic partition function

Let us derive expressions for these partition functions, one by one.

### I. Translational partition functions

You know that translational energy has three components, one each in x, y and z directions. Each of these contribute to the translational partition function. To work out the expression, we will consider particle in one-dimensional case and use the energy expression from particle in a one-dimensional box system which you would have studied in your earlier classes. You would recall that for a particle of mass $m$ confined into a one-dimensional box of length $l$, the energy of the particle is given as

$$\varepsilon_{n,trans} = \frac{n^2h^2}{8ml^2} \, n = 1,2,3\dots \quad \dots (4.74)$$

Here, n is the quantum number. The energy of the lowest energy state $n$ =1, is equal to

$$\varepsilon_{n,trans} = \frac{h^2}{8ml^2} \quad \dots (4.75)$$

In case of Boltzmann distribution, the energy of the lowest level is taken as zero. Therefore, the energy of the $n^{th}$ energy level must be scaled relative to the lowest level. This implies that the energy of $n^{th}$ energy relative to the lowest energy state is equal to

$$\varepsilon_{n,trans} = (n^2-1)\,\varepsilon_{1,trans} \qquad \dots (4.76)$$

The translational partition function in x-direction can thus be written as

$$q_{x,trans} = \sum_n e^{-\frac{(n^2-1)\varepsilon_{1,trans}}{kT}} \qquad \dots (4.77)$$

The summation is over all the energy levels. Since the translational energy levels are very close to each other, they can be taken to vary continuously. Hence, we can replace summation by integration. Therefore,

$$q_{x,trans} = \int_1^{\infty} e^{-\frac{(n^2-1)\varepsilon_{1,trans}}{kT}}\,dn \qquad \dots (4.78)$$

To solve the above integral, we use the approximations that $n^2-1 \approx n^2$ and the lower limit of integral is changed to zero. Therefore,

$$q_{x,trans} = \int_0^{\infty} e^{-\frac{n^2\varepsilon_{1,trans}}{kT}}\,dn \qquad \dots (4.79)$$

Let us substitute, $\frac{n^2\varepsilon_{1,trans}}{kT} = x^2$ … (4.80)

Differentiating and simplifying, we get

$$dn = \left(\frac{kT}{\varepsilon_{x,trans}}\right)^{1/2} dx \qquad \dots (4.81)$$

Substituting in Eq. (4.79) we get

$$q_{x,trans} = \left(\frac{kT}{\varepsilon_{x,trans}}\right)^{1/2} \int_0^{\infty} e^{-x^2}\,dx \qquad \dots (4.82)$$

The integral here is a standard form of the integral, viz., $\int_0^{\infty} e^{-x^2}dx$ which is equal to $\frac{\pi^{1/2}}{2}$. Substituting in Eq. (4.82) we get

$$q_{x,trans} = \left(\frac{kT}{\varepsilon_{x,trans}}\right)^{1/2} \frac{\pi^{1/2}}{2} \qquad \dots (4.83)$$

Substituting the expression for $\varepsilon_{x,trans}$ from Eq. (4.74) in Eq. (4.83)we get

$$q_{x,trans} = \left(\frac{kT8ml^2}{h^2}\right)^{1/2} \frac{\pi^{1/2}}{2} \qquad \dots (4.84)$$

On simplification, we get

$$q_{x,trans} = \left(\frac{2\pi kTm}{h^2}\right)^{1/2} l \qquad \dots (4.85)$$

This is the expression for the translational partition function for x- direction. We will have similar expressions for the y- and z- direction. The total translational partition function is equal to the product of the partition functions in three directions, viz.,

$$q_{trans} = q_{x,trans} \cdot q_{y,trans} \cdot q_{z,trans} \qquad \text{… (4.86)}$$

Let us assume that the translational length in the x, y and z directions be $l, b, \text{and}\, h$ respectively. Substituting the expression for the translational partition function for different directions, we get

$$q_{trans} = \left(\frac{2\pi kTm}{h^2}\right)^{1/2} l \left(\frac{2\pi kTm}{h^2}\right)^{1/2} b \left(\frac{2\pi kTm}{h^2}\right)^{1/2} h \qquad \text{… (4.87)}$$

Simplifying, we get

$$q_{trans} = \left(\frac{2\pi kTm}{h^2}\right)^{3/2} lbh \qquad \text{… (4.88)}$$

Since, $lbh$ is equal to the volume, *V,* we can write

$$q_{trans} = \left(\frac{2\pi kTm}{h^2}\right)^{3/2} V \qquad (4.89)$$

Thus, the translational partition function depends on the mass of the particle, temperature, and the volume of the system. Let us take an example

**Example 4.4**: 1 mole of Neon gas (molar mass 20.1797 g mol$^{-1}$) occupies a volume of 0.0245 m$^3$ at 298 K. Calculate the translational partition function for the system.

**Solution**: The translational partition function is given by the following expression.

$$q_{trans} = \left(\frac{2\pi kTm}{h^2}\right)^{3/2} V$$

Most of the parameters are given or known, however we need to calculate the value of mass of the neon atom to use the expression.

$$\text{Mass} = \frac{\text{Molar mass}}{\text{Avagadro's number}} = \frac{0.0201797\,\text{kg mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 3.351 \times 10^{-26}\,\text{kg}$$

Substituting the values in the expression, we get

$$q_{trans} = \left[\frac{2(3.1419)(1.381 \times 10^{-23}\,\text{JK}^{-1})(298\text{K})(3.351 \times 10^{-26})}{(6.626 \times 10^{-34}\,\text{J.s})^2}\right]^{3/2} \times 0.0245\,\text{m}^3$$

Solving the expression we get

$$q_{trans} = 2.148 \times 10^{24}$$

### II. Rotational partition functions

$$q_{rot} = \sum_i g_{i,rot} e^{-\frac{\varepsilon_{i,rot}}{kT}} \qquad \dots (4.90)$$

Recall that the rotational energy for linear molecule is given as

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2I} \qquad \dots (4.91)$$

Here *J* = 0, 1, 2, …are the rotational quantum numbers, $\hbar$ cross is action constant ( $h/2\pi$ ) and $I$ is the moment of inertia. Since the lowest rotational energy is zero, there is no need to scale $\varepsilon_{i,rot}$ with respect to lowest energy level. Further, you know that the degeneracy of rotational level *J is given as*

$$g_{\text{J}} = 2J+1 \qquad \dots (4.92)$$

Substituting the values of $\varepsilon_{\text{J}}$ , and $g_{\text{J}}$ *,the expression for* $q_{rot}$ becomes

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)\cdot \exp\left[-\frac{J(J+1)\hbar^2/2I}{kT}\right] \qquad \dots (4.93)$$

Rearranging, we get

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)\cdot \exp\left[-\frac{J(J+1)\hbar^2}{2IkT}\right] \qquad \dots (4.94)$$

You may note that at all the constants except $T$ and $J$ in the exponent can be combined to give a constant having units of temperature. This constant is called rotational temperature $\theta_r$and is defined as

$$\theta_r \equiv \frac{\hbar^2}{2Ik} \qquad \dots (4.95)$$

Substituting the new constant, the equation becomes

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)\cdot e^{-J(J+1)\theta_r/T} \qquad \dots (4.96)$$

At high temperatures, the fraction $\theta_r/T$ is small. Also, the difference between the consecutive energy levels is very small **a**t room temperature. For most of the cases, *kT* is much larger than the energy difference thereby many rotational levels are occupied. Therefore, we can replace the summation in Eq. (4.96) by integration i.e.,

$$q_{\text{rot}} = \int_{J=0}^{\infty} (2J+1)\cdot e^{-J(J+1)\theta_r/T} dJ \qquad \dots (4.97)$$

Solving this integral is not straight forward as the quantum number J appears in body as well as the exponent in the integral term. To solve it we make a small substitution as

$$x = J^2 + J \qquad \dots (4.98)$$

Taking derivative, we get

$$dx = (2J+1)dJ \qquad \dots (4.99)$$

Rearranging Eq. (4.97) we get

$$q_{\text{rot}} = \int_{J=0}^{\infty} e^{-J(J+1)\theta_r/T}[(2J+1)]\,dJ \qquad \dots (4.100)$$

Making the substitution we get

$$q_{\text{rot}} = \int_{J=0}^{\infty} e^{-x\theta_r/T}dx \qquad \dots (4.101)$$

This is a standard integral of the type $\left(\int_0^{\infty} e^{-ax}dx\right)$ having a known solution $\left(1/a\right)$. Using this solution, we get

$$q_{\text{rot}} = \frac{T}{\theta_r} \qquad \dots (4.102)$$

Substituting the value of $\theta_r$ we get

$$q_{\text{rot}} = \frac{8\pi^2 IkT}{h^2} \qquad \dots (4.103)$$

### III. Vibrational partition function

We can write the general expression for vibrational quantum number as

$$q_{vib} = \sum_i g_{i,vib}\, e^{-\frac{\varepsilon_{i,vib}}{kT}} \qquad \dots (4.104)$$

Let us take only the case of harmonic vibrations. The energy of a given vibrational level is

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu \qquad \dots (4.105)$$

Here, $v$ = 0, 1, 2, 3….

Energy of the lowest level, $\varepsilon_0 = \frac{1}{2}h\nu$. The difference between two consecutive energy levels is $h\nu$.

$$q_{vib} = e^{-\frac{\left(0+\frac{1}{2}\right)h\nu}{kT}} + e^{-\frac{\left(1+\frac{1}{2}\right)h\nu}{kT}} + e^{-\frac{\left(2+\frac{1}{2}\right)h\nu}{kT}} + \dots \qquad \dots (4.106)$$

Simplifying, we get

$$q_{vib} = e^{-\frac{h\nu}{2kT}} + e^{-\frac{3h\nu}{2kT}} + e^{-\frac{5h\nu}{2kT}} + \dots \qquad \dots (4.107)$$

This can be written as

$$q_{vib} = e^{-\frac{h\nu}{2kT}}\left(1 + e^{-\frac{h\nu}{kT}} + e^{-2\frac{h\nu}{kT}} + e^{-3\frac{h\nu}{kT}} + \dots\right) \qquad \dots (4.108)$$

Let $\frac{h\nu}{kT} = x$, we can write

$$q_{vib} = e^{-\frac{h\nu}{2kT}}\left(1+e^{-x}+e^{-2x}+e^{-3x}+\ldots\right) \qquad \ldots (4.109)$$

The term in the bracket is a series expansion for $\left(\dfrac{1}{1-e^{-x}}\right)$

Substituting back and replacing x we get

$$q_{vib} = \left(\frac{1}{1-e^{-\frac{h\nu}{kT}}}\right) = \frac{e^{-\frac{h\nu}{2kT}}}{1-e^{-\frac{h\nu}{kT}}} \qquad \ldots (4.110)$$

In this expression we have not scaled the energy of the upper level to $\varepsilon_0$. Thus, Eq. (4.94) includes zero-point energy. When the zero-point energy is scaled to zero as we had done for translational energy, vibrational partition function becomes

$$q_{vib} = \frac{1}{1-e^{-(h\nu/kT)}} \qquad \ldots (4.111)$$

### IV. Electronic partition function

The electronic partition function is given by the following expression.

$$q_{el} = \sum_i g_{i,el}\, e^{-e_{i,el}/kT} \qquad \ldots (4.112)$$

Let us learn about electronic partition function with the help of an example.

**Example 4.5**: The energies and degeneracies of first three electronic states of an atom from the first period are given below:

| State | Energy (J) | Degeneracy |
|---|---|---|
| 1 | 0 | 1 |
| 2 | $3.26 \times 10^{-22}$ | 3 |
| 3 | $8.64 \times 10^{-22}$ | 5 |

Calculate the electronic partition function at 300 K.

**Solution**: As per Eq. (4.112) the electronic partition function is given as

$$q_{el} = \sum_i g_{i,el}\, e^{-e_{i,el}/kT}$$

Expanding the expression for the first three energy levels we can write

$$q_{el} = g_{1,el}\, e^{-\varepsilon_{1,el}/kT} + g_{2,el}\, e^{-\varepsilon_{2,el}/kT} + g_{3,el}\, e^{-\varepsilon_{3,el}/kT}$$

Let us first calculate the value of $kT$ that appears in all the terms

$$kT = 1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\times300\,\mathrm{K} = 4.143\times10^{-21}\,\mathrm{J}$$

Substituting the values of degeneracies, energies and the $kT$ term, we get

$$q_{el} = 1e^{-\frac{0}{4.143\times10^{-21}\,\mathrm{J}}} + 3e^{-\frac{3.26\times10^{-22}\,\mathrm{J}}{4.143\times10^{-21}\,\mathrm{J}}} + 5e^{-\frac{8.64\times10^{-22}\,\mathrm{J}}{4.143\times10^{-21}\,\mathrm{J}}}$$

Simplifying, we get

$$q_{el} = 1e^{0} + 3e^{-0.079} + 5e^{-0.209}$$

Solving we get,

$$q_{el} = 1 + (3 \times 0.924) + (5 \times 0.811) = 1 + 2.772 + 4.055 = 7.827$$

Thus, the electronic partition function would be =7.827.

Generally, the gap between the ground state and first excited state is large and most of the molecules exist in ground electronic energy state. That is, in the dominant configuration, only one electronic state is present. Therefore, we can write the partition function as

$$q_{el} = g_{el} \quad \text{… (4.113)}$$

Here $g_{el}$ is the degeneracy of the ground electronic energy state. If the degeneracy of the ground state happens to be one, the electronic partition function simply is:

$$q_{el} = 1 \quad \text{… (4.114)}$$

Having learnt about partition function, its significance and different components let us take an important concept of canonical ensemble.However, before that answer the following simple questions.

*SAQ 5*

Calculate the rotational partition function at 500 K for a diatomic molecule having moment of inertia of $2.69 \times 10^{-43}$ kg m².

*SAQ 6*

The volume of 1 mole of a gas (molar mass 39.947 g mol$^{-1}$) at $10^{5}$ Pa and 400K is 0.033258m$^{3}$. Calculate the translational partition function for the system.

## 4.4 CANONICAL ENSEMBLE

In the previous sections we have done statistical studies on a single system which is a collection of many identical particles. A system is also known as **assembly**. A group or collection of assemblies or systems is known as an ensemble. We had considered the total energy of the system to be fixed. However, in case of ensemble, the energy of the systems in contact with the surroundings will fluctuate. Since different parts of the ensemble can also exchange energy with each other, the energy of the ensemble will fluctuate. So, in such cases we cannot assume that the energy is fixed. However, we can fix the temperature of the ensemble by keeping it in contact with the large heat reservoir. The word canonical means according to the rule. The ensemble in which by rule number of molecules (*N*), volume (*V*) and the temperature (*T*) are kept constant is known as **canonical ensemble**. In canonical ensemble, all the systems are at the same temperature, pressure, and volume. The total energy of the canonical ensemble is constant. However, the energies of the individual systems can be different. The energy of individual systems will be close to the average energy of the ensemble. In this section we will extend the statistical studies on a system to that of an ensemble.

The total number of particles in an ensemble = $\tilde{N}$

The number of particles in an ensemble with energy $E_i = \tilde{N}_i$

The weight of a configuration of ensemble with population $\tilde{N}_0, \tilde{N}_1, \tilde{N}_2, \tilde{N}_3, \ldots$ is given as

$$\tilde{W} = \frac{\tilde{N}!}{\tilde{N}_0!\,\tilde{N}_1!\,\tilde{N}_2!\,\tilde{N}_3!\ldots} \qquad \ldots (4.115)$$

Like Boltzmann distribution, **canonical distribution** for the dominant configuration of the ensemble with the constraints that the total energy of the ensemble, $\tilde{E}$ is constant and $\tilde{N}$ is also fixed can be written as

$$\frac{\tilde{N}_i}{\tilde{N}} = e^{\alpha}.e^{-\beta E_i} = \frac{e^{-\beta E_i}}{Q} \qquad \ldots (4.116)$$

$$Q = \sum_i e^{-\beta E_i} \qquad \ldots (4.117)$$

Here, $Q$ is the **canonical partition function**,

**Relation between molecular partition function and canonical partition function**

Let us consider a collection of $N$ molecules that are not interacting with each other, that is, they are independent of each other. The total energy of the collection of molecules in a state is the sum of the energies of individual molecules in that state. The total energy of the collection in $i^{th}$ state is written as

$$E_i = \varepsilon_i(1) + \varepsilon_i(2) + \varepsilon_i(3) + \ldots + \varepsilon_i(N) \qquad \ldots (4.118)$$

The partition function of the collection is written as

$$Q = \sum_i e^{-\beta\{\varepsilon_i(1) + \varepsilon_i(2) + \ldots + \varepsilon_i(N)\}} \qquad \ldots (4.119)$$

This expression can be expanded for each energy state as

$$Q = e^{-\beta\{\varepsilon_1(1) + \varepsilon_1(2) + \ldots + \varepsilon_1(N)\}} + e^{-\beta\{\varepsilon_2(1) + \varepsilon_2(2) + \ldots + \varepsilon_2(N)\}} + \ldots \qquad \ldots (4.120)$$

Expanding the above equation further and taking all the terms of one molecule together we get

$$Q = \{e^{-\beta\{\varepsilon_1(1)} + e^{-\beta\{\varepsilon_2(1)} + \ldots\}\,.\,\{e^{-\beta\{\varepsilon_1(2)} + e^{-\beta\{\varepsilon_2(2)} + \ldots\}\ldots\{e^{-\beta\varepsilon_1(N)} + e^{-\beta\varepsilon_2(N)} + \ldots$$

$$Q = \left\{\sum_i e^{-\beta\{\varepsilon_1(1)}\right\}.\left\{\sum_i e^{-\beta\{\varepsilon_i(2)}\right\}.\left\{\sum_i e^{-\beta\{\varepsilon_i(3)}\right\}\ldots\left\{\sum_i e^{-\beta\{\varepsilon_i(N)}\right\} \qquad \ldots (4.121)$$

The terms inside the curly brackets are the partition functions of the individual molecules. Therefore,

$$Q = q(1).q(2)...q(N) \qquad \text{… (4.122)}$$

For distinguishable molecules of the same type, all the molecular partition functions will be same. Therefore,

$$Q = q^N \text{ for distinguishable particles} \qquad \text{… (4.123)}$$

When the particles are indistinguishable, the above expression is modified as

$$Q = \frac{q^N}{N!} \text{ for indistinguishable particles} \qquad \text{… (4.124)}$$

## 4.5 THERMODYNAMIC PROPERTIES AND PARTITION FUNCTION

You may recall that we stated that statistical thermodynamics acts as a bridge between the microscopic properties of atoms and molecules and the thermodynamic properties of bulk matter. Also, the major aim of statistical thermodynamics is to be able to calculate the thermodynamic properties of systems using the mathematics of statistics. In the previous sections, you have studied about the molecular partition function, and canonical partition function. We are now equipped to take up the calculation of thermodynamic properties of a system from partition functions. However, we will not be taking these in detail here. We will just demonstrate the approach by taking the case of calculation of average energy of a molecule in terms of molecular partition function.

### 4.5.1 Average Energy of the Molecule

In this section, we will write the energy of the molecule in terms of partition function. For a collection of *N* identical molecules, if the energy of the system is *E*, then the average energy of one molecule is obtained by dividing the energy of the system by the total number of molecules in the system i.e.,

$$\langle \varepsilon \rangle = \frac{E}{N} \qquad \text{… (4.125)}$$

You have learnt above that at equilibrium the energy distribution is given by Boltzmann distribution. The total energy is written as,

$$\sum_i N_i \varepsilon_i = E \qquad \text{… (4.126)}$$

And $$N_i = \frac{Ne^{-\varepsilon_i/kT}}{q} \qquad \text{… (4.127)}$$

Therefore,

$$\langle \varepsilon \rangle = \frac{\sum_i N_i \varepsilon_i}{N} = \frac{1}{q}\sum_i \varepsilon_i e^{-\varepsilon_i/kT} \qquad \text{… (4.128)}$$

Using some mathematical rearrangement,

$$\frac{de^{-\beta\varepsilon_i}}{d\beta} = \varepsilon_i e^{-\beta\varepsilon_i} \qquad \ldots (4.129)$$

Therefore,

$$\langle\varepsilon\rangle = -\frac{1}{q}\sum_i \frac{de^{-\beta\varepsilon_i}}{d\beta} = -\frac{1}{q}\frac{d}{d\beta}\sum_i e^{-\beta\varepsilon_i} \qquad \ldots (4.130)$$

$$\langle\varepsilon\rangle = -\frac{1}{q}\frac{dq}{d\beta} = \frac{d\ln q}{d\beta} \qquad \ldots (4.131)$$

Recall that β = 1/*kT*. So, the differential is in Eq. (4.131) is showing the variation of partition function with temperature. During the differentiation, other parameters which may affect the partition function, for example, volume are kept constant. Also, in partition function expression we take the lowest energy, $\varepsilon_0$(which is equal to the zero-point energy) as zero. Therefore, the zero-point energy has to be included in the calculation of average energy of the molecule. After applying these modifications, Eq. (4.131) is written as

$$\langle\varepsilon\rangle = \varepsilon_0 - \left(\frac{d\ln q}{d\beta}\right)_V \qquad \ldots (4.132)$$

Let us sum up what all we have discussed in this unit.

## 4.6 SUMMARY

In this unit we continued our discussion on statistical thermodynamics and began the unit by taking up Boltzmann distribution function. The discussion was initiated by extending the concept permutation and configuration to the chemical systems. In this process we introduced and explained the concepts of microstates and configurations. The total number of microstates associated with a given configuration is known as the weight of the configuration and is a measure of the probability of the configuration to be observed. The configuration with maximum weight is known as dominant configuration. With an increase in the size of the system the dominant configuration becomes the equilibrium configuration.

In the process of deriving expression for the Boltzmann's distribution function we introduced the crucial concept of partition function and outlined its significance. Thereafter we took up the formulation of partition functions for different types of energies of the system. it was followed by the introduction of the idea of canonical ensemble. Having learnt Boltzmann's distribution and partition functions in details we took up the calculation of the thermodynamic properties of a system from partition functions.

## 4.7 TERMINAL QUESTIONS

1. Define the following:
   a) Microstates
   b) Weight of a configuration

c) Dominant configuration

2. Consider the distribution of five quanta ($E_0$) of energy amongst three distinguishable quantum particles having four energy states of 0, $E_0$, $2E_0$ and $3E_0$ available. Identify different configurations and calculate their weights.

3. Give the constraints applied for Boltzmann distribution.

4. Which among $N_2$ and $H_2$ will have higher translational partition function? Give reason.

5. Calculate the electronic partition function at 300 K for a system using its first three doubly degenerate energy levels with energies as 0, $1\text{x}10^{-21}$ J and $2.5\text{x}10^{-21}$ J respectively.

6. The rotational temperature for HI molecule is 9.43 K. Calculate the moment of inertia for HI.

## 4.8 ANSWERS

### Self-Assessment Questions

1. The arrangements of particles in different energy states are called configurations whereas the specific arrangements (permutations) of particles in each configuration are known as microstates.

2. The possible distributions for 7 distinguishable particles among 4 energy levels under the constraint of total energy being 3 quanta along with their weights and ratios $W/W_{tot}$ are as under.

| Dist. | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $W$ | $W/W_{tot}$ |
|---|---|---|---|---|---|---|
| 1. | 6 | 0 | 0 | 1 | 7 | 0.08 |
| 2. | 5 | 1 | 1 | 0 | 42 | 0.50 |
| 3. | 4 | 3 | 0 | 0 | 35 | 0.42 |
| | | | | Total | 84 | 1.00 |

3. The possible distributions and the corresponding weights and probabilities for one hundred molecules under given set of conditions are

| Dist. | $N_0$ | $N_1$ | $N_2$ | $N_3$ | $N_4$ | $N_5$ | $W$ | $W/W_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 1. | 99 | 0 | 0 | 0 | 0 | 1 | 100 | $1.088\text{x}10^{-8}$ |
| 2. | 98 | 1 | 0 | 0 | 1 | 0 | 9900 | $1.077\text{x}10^{-4}$ |
| 3. | 98 | 0 | 1 | 1 | 0 | 0 | 9900 | $1.077\text{x}10^{-4}$ |
| 4. | 97 | 2 | 0 | 1 | 0 | 0 | 485100 | $5.27\text{x}10^{-3}$ |
| 5. | 97 | 1 | 2 | 0 | 0 | 0 | 485100 | $5.27\text{x}10^{-3}$ |
| 6. | 96 | 3 | 1 | 0 | 0 | 0 | 15654900 | 0.1703 |
| 7. | 95 | 5 | 0 | 0 | 0 | 0 | 75287520 | **0.8189** |
| Total | | | | | | | 91932520 | 1.00 |

4. i) We know that according to Boltzmann's law

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}$$

Substituting the values in the expression for denominator gives

$$\sum_i e^{-\varepsilon_i/kT} = e^0 + e^{-\varepsilon_1/kT} = 1 + e^{-\frac{1.6\times10^{-20}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(300K)}}$$

Solving, we get

$$\sum_i e^{-\varepsilon_i/kT} = 1 + e^{-\frac{1.6\times10^{-20}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(300K)}} = 1 + e^{-3.862} = 1.021$$

The fraction of molecules in the excited state can then be calculated as

$$\frac{N_i}{N} = \frac{e^{-\frac{1.6\times10^{-20}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(300K)}}}{1.021} = \frac{0.021}{1.021} = 0.0206$$

Thus, fraction of molecules in the excited state at 300 K = 0.0206. This means about 2.06% of the molecules will be in excited state.

ii) For 1000K

Again, substituting the values in the expression for denominator gives

$$\sum_i e^{-\varepsilon_i/kT} = e^0 + e^{-\varepsilon_1/kT} = 1 + e^{-\frac{1.6\times10^{-20}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(1000K)}}$$

Solving, we get

$$\sum_i e^{-\varepsilon_i/kT} = 1 + e^{-\frac{1.6\times10^{-20}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(1000K)}} = 1 + e^{-1.1586} = 1.3139$$

The fraction of molecules in the excited state can then be calculated as

$$\frac{N_i}{N} = \frac{e^{-\frac{8.0\times10^{-21}\,\text{J}}{(1.381\times10^{-23}\,\text{JK}^{-1})(300K)}}}{1.3139} = \frac{0.3139}{1.3139} = 0.2389$$

That is, the fraction of molecules in the excited state at 1000 K = 0.2389 implying that23.89 % of the molecules will be in excited state.

iii) You may note that the given system is like the one in the example but with the energy of the excited state is double of that in the example. We find that there is a significant decrease (from 12.7% to 2.06 %) in the population of the excited state. It is in accordance with the Boltzmann's law as the energy of excited state increases its population decreases.

In the second case the temperature was increased and this lead to an increase (from 2.06 % at 300K to 23.89% at 1000K) in thepopulation of the excited state

5. As per Eq. (4.103) the rotational partition function is given as

$$q_{\mathrm{rot}} = \frac{8\pi^2 IkT}{h^2}$$

Given: $I = 2.69\times10^{-43}\, kg\, m^2$ and $T = 500K$

Substituting the values, we get

$$q_{\mathrm{rot}} = \frac{8(3.1419)^2(2.69\times10^{-43}\, kg\, m^2)(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(500\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J.s})^2}$$

Solving we get

$$q_{\mathrm{rot}} = 3.34\times10^5$$

6. The translational partition function is given by the following expression.

$$q_{trans} = \left(\frac{2\pi kTm}{h^2}\right)^{3/2} V$$

Most of the parameters are given or known, however we need to calculate the value of mass of the gas molecule to use the expression.

$$mass = \frac{\text{Molar mass}}{\text{Avagadro's number}} = \frac{0.039947\, kg\, mol^{-1}}{6.022\times10^{23}\, mol^{-1}} = 6.634\times10^{-26}\, kg$$

Substituting the values in the expression, we get

$$q_{trans} = \left[\frac{2(3.1419)(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(400\mathrm{K})(6.634\times10^{-26})}{(6.626\times10^{-34}\,\mathrm{J.s})^2}\right]^{3/2} \times 0.03326\, m^3$$

Solving the expression we get

$$q_{trans} = 2.154\times10^{26}$$

## Terminal Questions

1. a. Microstates are the permutations possible for a given configuration

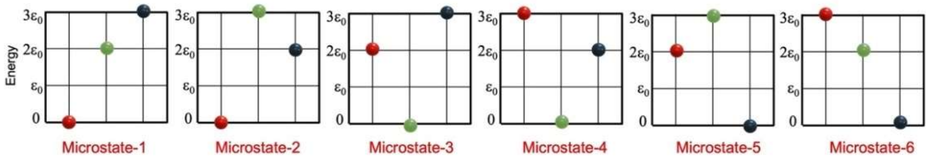
   b. Weight of a configuration is the number of microstates possible in each configuration

$$W = \frac{N!}{N_0!N_1!N_2!N_3!\ldots}$$

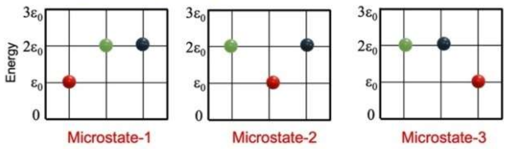
c. Dominant configuration is the configuration of a system having maximum weight.

2. Under given conditions, three different configurations are possible for the given case. These are {1,0,1,1}, {0,1,2,0}, and {0,2,0,1} with respective number of microstates as 6,3 and 3.Thethreeconfigurations and corresponding microstates are given diagrammatically as

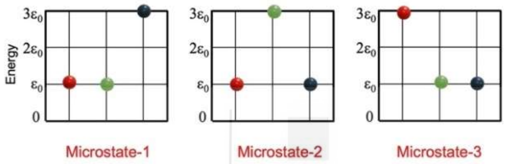
Configuration-I [1,0,1,1}


Energy
3ε0
2ε0
ε0
0
Microstate-1
Microstate-2
Microstate-3
Microstate-4
Microstate-5
Microstate-6

Configuration-II [0,1,2,0}


Energy
3ε0
2ε0
ε0
0
Microstate-1
Microstate-2
Microstate-3

Configuration-III [0,2,0,1}


Energy
3ε0
2ε0
ε0
0
Microstate-1
Microstate-2
Microstate-3

3. Constraints applied for Boltzmann distribution are that (i)the total population remains constant, if the population of one state increases, then the population of another state will decrease. (ii) if the population of a state changes, the total energy is not affected.

4. Translational partition function is given by the expression.

$$q_{trans} = \left(\frac{2\pi m}{\beta h}\right)^{3/2} V$$

For equal volumes of different gases, $q_{trans} \propto m^{3/2}$

Since, $m(H_2) < m(N_2)$, $q_{trans}(H_2) < q_{trans}(N_2)$

5. As per Eq. (4.112) the electronic partition function is given as

$$q_{el} = \sum_i g_{i,el} e^{-e_{i,el}/kT}$$

Expanding the expression for the first three energy levels we can write

$$q_{el} = g_{1,el} e^{-\varepsilon_{1,el}/kT} + g_{2,el} e^{-\varepsilon_{2,el}/kT} + g_{3,el} e^{-\varepsilon_{3,el}/kT}$$

Let us first calculate the value of $kT$ that appears in all the terms

$$kT = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 300\mathrm{K} = 4.143 \times 10^{-21}\,\mathrm{J}$$

Substituting the values of degeneracies, energies and the $kT$ term, we get

$$q_{el} = 2e^{-\frac{0}{4.143\times10^{-21}\,\mathrm{J}}} + 2e^{-\frac{1\times10^{-21}\,\mathrm{J}}{4.143\times10^{-21}\,\mathrm{J}}} + 2e^{-\frac{2.5\times10^{-21}\,\mathrm{J}}{4.143\times10^{-21}\,\mathrm{J}}}$$

Simplifying, we get

$$q_{el} = 2e^{0} + 2e^{-0.2414} + 2e^{-6.034}$$

Solving we get,

$$q_{el} = 1 + (2 \times 0.7855) + (2 \times 0.0019) = 2 + 1.571 + 0.0038 = 3.5748$$

Thus, the electronic partition function would be=3.5748.

6. As per Eq. (4.95), the rotational temperature is given as, $\theta_r \equiv \frac{\hbar^2}{2Ik}$

Rearranging we get, $I \equiv \frac{\hbar^2}{2\theta_r k}$

Substituting the values and solving gives

$$I \equiv \frac{(6.626 \times 10^{-34}\,\mathrm{J.s})^2}{(2 \times 3.1419)^2\, 2(9.3K)(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})} = 4.33 \times 10^{-47}\, kg\, m^2$$